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Source Category Report

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NONFERROUS INDUSTRY PARTICULATE EMISSIONS: SOURCE CATEGORY REPORT

by

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The report gives results of the development of particulate emission factors based on cutoff size for inhalable particles for the nonferrous industry. After a review of available information characterizing particulate emissions from nonferrous plants, the data were summarized and rated in terms of reliability. Size specific emission factors were developed from these data for the major processes used in the manufacture of nonferrous metals. A detailed process description is presented with emphasis on factors affecting the generation of emissions. A replacement for Sections 7.1 (Primary Aluminum Production), 7.3 (Primary Copper Smelting), 7.6 (Primary Lead Smelting), 7.7 (Primary Zinc Smelting), and 7.11 (Secondary Lead Smelting) of EPA report AP-42, A Compilation of Air Pollutant Emissions Factors, was prepared, containing the size specific emission factors developed during the program.

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ABSTRACT

The objective of this study was to develop particulate emission factors based on cutoff size for inhalable particles for the nonferrous industry. After a review of available information characterizing particulate emissions from nonferrous plants, the data were summarized and rated in terms of reliability. Size specific emission factors were developed from these data for the major processes used in the manufacture of nonferrous metals. A detailed process description was presented with empnasis on factors affecting the generation of emissions. A replacement for Sections 7.1 (Primary Aluminum Production), 7.3 (Primary Copper Smelting), 7.6 (Primary Lead Smelting), 7.7 (Primary Zinc Smelting), and 7.11 (Secondary Lead Smelting) of EPA report AP-42, A Compilation of Air Pollutant Emissions Factors, was prepared, containing the size specific emission factors developed during this program.

CONTENTS

Page

Abstract ii
Figures vi
Tables x

1 INTRODUCTION 1

2 PRIMARY ALUMINUM INDUSTRY 8

2.1 OVERVIEW 8

2.1.1 Aluminum Production Process 11
2.1.2 Particulate Emission Sources 19
2.1.3 Particulate Emission Controls 20

2.2 ALUMINUM INDUSTRY EMISSION FACTORS 21

2.2.1 Data Review 23
2.2.2 Data Analysis 30

2.3 CHEMICAL CHARACTERIZATION 39

3 PRIMARY COPPER INDUSTRY 40

3.1 OVERVIEW 40

3.1.1 Copper Production Process 43
3.1.2 Particulate Emission Sources 55
3.1.3 Particulate Emissions Controls 58

3.2 COPPER INDUSTRY EMISSION FACTORS 61

3.2.1 Data Review 61
3.2.2 Data Analysis 67

3.3 CHEMICAL CHARACTERIZATION 69

4 PRIMARY LEAD PROCESSING 81

4.1 PRIMARY LEAD PROCESSING INDUSTRY 81

4.1.1 Overview 81
4.1.2 Primary Lead Smelting and Refining Process 82

CONTENTS (Concluded)

Page

4.1.3 Particulate Emission Sources 88
4.1.4 Particulate Emission Controls 90

4.2 PRIMARY LEAD PROCESSING EMISSION FACTORS 91

4.2.1 Data Review 91
4.2.2 Data Analysis 106

4.3 CHEMICAL CHARACTERIZATION 114

5 SECONDARY LEAD PROCESSING 117

5.1 OVERVIEW 117

5.1.1 Secondary Lead 119
5.1.2 Particulate Emission Sources 124
5.1.3 Particulate Emissions Controls 125

5.2 SECONDARY LEAD PROCESSING EMISSION FACTORS 126

5.2.1 Data Review 126
5.2.2 Data Analysis 137

5.3 CHEMICAL CHARACTERIZATION 140

6 PRIMARY ZINC PROCESSING 145

6.1 OVERVIEW 145

6.1.1 Primary Zinc Process 147
6.1.2 Particulate Emission Sources 155
6.1.3 Particulate Emission Controls 155

6.2 PRIMARY ZINC PROCESSING EMISSION FACTORS 156

6.2.1 Data Review 156
6.2.2 Data Analysis 161

6.3 CHEMICAL CHARACTERIZATION 161

CONTENTS (Concluded)

Page

7 PROPOSED AP-42 SECTIONS 165

AP-42 Section 7.1 - Primary Aluminum Production. 166
AP-42 Section 7.3 - Primary Copper Smelting. 177
AP-42 Section 7.6 - Primary Lead Smelting. 196
AP-42 Section 7.11 - Secondary Lead Processing 212
AP-42 Section 7.7 - Primary Zinc Smelting. 223

References for Sections 1 to 6. 232

FIGURES

Number Page

1 Distribution of U.S. bauxite and alumina supply and aluminum plant capacities, 1981 10

2 Aluminum production process flow diagram. 12

3 Aluminum reduction cell diagram 13

4 Flow diagram for preparation of prebake anodes. 16

5 Particle size distribution for fugitive roof monitor emissions from the Kaiser Mead prebake aluminum plant . . . 26

6 Average B-rated particle size distribution for fugitive roof monitor emissions from three prebake aluminum. 32

7 Particle size distribution for fugitive emissions from a HSS aluminum plant. 33

8 B-rated particle size distribution for primary uncontrolled emissions from a HSS reduction aluminum plant 34

9 Cumulative emission factors less than stated particle size for fugitive emissions from prebake aluminum cells. 36

10 Cumulative emission factors less than stated particle size for fugitive emissions from HSS aluminum cells. 37

11 Cumulative emission factors less than stated particle size for primary emissions from HSS reduction cells. 38

12 Generalized copper production process flow diagram. 44

13 Sources of emissions in conventional copper smelting and refining. 56

14 Cumulative emission factors less than stated particle size for fugitive emissions from reverberatory furnace matte tapping operations. 70

15 Cumulative emission factors less than stated particle size for fugitive emissions from reverberatory furnace matte slag tapping operations. 71

16 Cumulative size specific emission factors for emissions from multiple hearth roaster and reverberatory smelter 74

FIGURES (Continued)

Number Page

17 Cumulative size specific emission factors for emissions from reverberatory smelting 75

18 Cumulative size specific emission factors for emissions from copper converting. 76

19 Cumulative size specific emission factors for fugitive emissions from converter slag and copper blow operations. . 77

20 Typical primary lead smelter process schematic. 84

21 Lead updraft sinter machine 85

22 Primary processing lead blast furnace 87

23 Primary processing lead reverberatory furnace 89

24 A-rated particle size distribution for controlled primary lead processing blast furnace flue gases. 93

25 B-rated particle size distribution for fugitive emissions from primary lead processing ore storage. 94

26 B-rated particle size distribution for fugitive emissions from a primary lead processing sinter machine 95

27 B-rated particle size distribution for fugitive emissions from a primary lead processing blast furnace. 96

28 B-rated particle size distribution for fugitive emissions from a primary lead smelting dross kettle 97

29 B-rated particle size distribution for fugitive emissions from a primary lead processing reverberatory furnace. . . . 98

30 Cumulative size-specific emission factors for baghouse controlled emissions from a blast furnace 107

31 Cumulative size-specific emission factors for uncontrolled ore storage fugitive emissions. 108

32 Cumulative size-specific emission factors for uncontrolled sinter machine fugitive emissions 109

33 Cumulative size-specific emission factors for uncontrolled blast furnace fugitive emissions. 110

FIGURES (Continued)

Number		Page
34	Cumulative size-specific emission factors for uncontrolled dross kettle fugitive emissions	111
35	Cumulative size-specific emission factors for uncontrolled reverberating furnace fugitive emissions.	112
36	Process schematic secondary lead smelting and refining. . .	120
37	Lead reverberatory furnace.	122
38	Secondary processing lead blast furnace	123
39	Particle size distribution for uncontrolled emissions from blast furnace ventilation gases	134
40	Particle size distribution for uncontrolled and controlled emissions from a blast furnace.	135
41	Cumulative emission factors less than stated particle size for baghouse controlled secondary lead processing blast furnace process flue gases.	138
42	Cumulative emission factors less than stated particle size for controlled and uncontrolled blast furnace ventilation emissions	139
43	Primary zinc processing schematic	148
7.1-1	Schematic diagram of aluminum production process.	168
7.1-2	Emission factors less than stated particle size for fugitive emissions from prebaked aluminum cells.	172
7.1-3	Emission factors less than stated particle size for fugitive emissions from HSS aluminum cells	173
7.1-4	Cumulative emission factors less than stated particle size for primary emissions from HSS reduction cells.	174
7.3-1	Typical primary copper smelter process.	179
7.3-2	Size specific emission factors for multiple hearth roaster and reverberatory smelter	185
7.3-3	Size specific emission factors for reverberatory smelting .	186

FIGURES (Concluded)

Number **Page**

7.3-4 Size specific emission factors for copper converting. . . . 187

7.3-5 Size specific fugitive emission factors for reverberatory furnace matte tapping operations 189

7.3-6 Size specific fugitive emission factors for reverberatory furnace slag tapping operations 190

7.3-7 Size specific fugitive emission factors for converter slag and copper blow operations. 191

7.6-1 Typical primary lead processing scheme. 198

7.6-2 Size specific emission factors for baghouse controlled blast furnace 203

7.6-3 Size specific uncontrolled fugitive emission factors for lead ore storage. 204

7.6-4 Size specific fugitive emission factors for uncontrolled sinter machine 205

7.6-5 Size specific lead fugitive emission factors for uncontrolled blast furnace 206

7.6-6 Size specific lead fugitive emission factors for uncontrolled dross kettle. 207

7.6-7 Size specific lead fugitive emission factors for unconrolled reverberating furnace 208

7.11-1 Typical secondary lead smelting and refining scheme 214

7.11-2 Emission factors less than stated particle size for baghouse controlled blast furnace flue gases 218

7.11.3 Emission factors less than stated particle size for uncontrolled and baghouse controlled blast furnace ventilation . 219

7.7-1 Typical primary zinc smelting process 225

TABLES

Number		Page
1	Primary Aluminum Producers in the United States 1984 . . .	9
2	Summary of Air Pollution Characteristics and Control . . .	22
3	Particulate Emission Capture by Cell Hoods	23
4	Summary of Acceptable Data	25
5	Summary of Particulate Emission Test Data	31
6	Emission Factors for Primary Aluminum Production Processes	35
7	Emission Factors and Particle Size Distribution for Fugitive (Roof Monitor) Emissions from Prebake Aluminum Cells	36
8	Emission Factors and Particle Size Distribution for Fugitive (Roof Monitor) Emissions from HSS Aluminum Cells	37
9	Emission Factors and Particle Size Distribution for Primary Emissions from HSS Reduction Cells	38
10	U.S. Primary Copper Producers	41
11	Summary of Kennecott Company Data	62
12	Summary of ASARCO Corporation Data	64
13	Summary of Phelps Dodge Data	66
14	Summary of Kennecott Copper Data	66
15	Summary of ASARCO Corporation Data	67
16	Summary of Phelps Dodge-Ajo Data	68
17	Summary of MAGMA Data	68
18	Factors and Particle Size Distribution for Fugitive Emissions from Reverberatory Furnace Matte Tapping Operations	70

TABLES (Continued)

Number Page

19 Emission Factors and Particle Size Distribution for Fugitive Emissions from Reverberatory Furnace Slag Tapping Operations 71

20 Emission Factors for Primary Copper Smelters 72

21 Fugitive Emission Factors for Primary Copper Smelters . . . 73

22 Cumulative Particle Size Distribution and Size Specific Emissions from Multiple Hearth Roaster and Reverberatory Smelter Operations 74

23 Cumulative Particle Size Distribution and Size Specific Emissions from Reverberatory Smelter Operations 75

24 Cumulative Particle Size Distribution and Size Specific Emissions from Copper Converting Operations 76

25 Cumulative Particle Size Distribution and Size Specific Emission Factors for Fugitive Emissions from Converter Slag and Copper Blow Operations 77

26 Weight Analysis of Uncontrolled Particulate Emissions from a Multiple Hearth Copper Roaster 79

27 Analysis of Particulates Emitted from a Reverberatory Furnace 79

28 Weight Analysis of Uncontrolled Particulate Emissions from Copper Converter Operations 80

29 U.S. Primary Lead Smelting and Refining Capacity 83

30 Summary of Particulate Emissions Tests for Primary Lead Processing 92

31 Point Source Particulate Emission Rate Test Data for Primary Lead Processing 99

32 Fugitive Particulate Emission Rate Test Data for Primary Lead Processing 100

33 Summary of A-Rated Data 101

TABLES (Continued)

Number		Page
34	Emission Factors and Particle Size Distribution for Baghouse Controlled Emissions from Blast Furnace Flue Gases	107
35	Emission Factors and Particle Size Distribution for Uncontrolled Ore Storage Fugitive Emissions	108
36	Emission Factors and Particle Size Distribution for Uncontrolled Sinter Machine Fugitive Emissions	109
37	Emission Factors and Particle Size Distribution for Uncontrolled Blast Furnace Fugitive Emissions	110
38	Emission Factors and Particle Size Distribution for Uncontrolled Dross Kettle Fugitive Emissions	111
39	Emission Factors and Particle Size Distribution for Uncontrolled Reverberating Furnace Fugitive Emissions . . .	112
40	Emission Factor Table for Primary Lead Processing	113
41	Typical Lead Ore Concentrate Chemical Analyses	115
42	Point Source Particulate Emissions Lead Content	116
43	Fugitive Emissions: Major Species by X-Ray Diffraction	116
44	Annual Consumption of Scrap Lead in the United States . . .	118
45	Summary of Particulate Emissions Tests for Secondary Lead Processing	127
46	Particulate Emission Rate Test Data	129
47	Summary of the B-Rated Data	131
48	Mass Emission Factor Data for Size-Specific Emission Factor Calculations	132
49	Emission Factors and Particle Size Distribution for Baghouse Controlled Emissions from Blast Furnace Flue Gases	138

TABLES (Continued)

Number Page

50 Emission Factors and Particle Size Distribution for Controlled and Uncontrolled Blast Furnace Ventilation Emissions 139

51 Particulate Emission Factor Table -- Secondary Lead Processing 141

52 Fugitive Emission Factors for Secondary Lead Processing 142

53 Crystalline Species Present in Flue Dust from a Secondary Lead Smelter 142

54 Chemical Composition of the Dust from a Secondary Lead Smelter 143

55 Lead Content of Particulate Emissions from Secondary Lead Smelting and Refining 143

56 Lead Emission Factor Table--Secondary Lead Smelting and Refining 144

57 Primary Zinc Processing Capacity 147

58 Summary of Particulate Emissions Tests -- Primary Zinc Processing 156

59 Total Particulate Emission Factor Data and Estimates -- Primary Slab Zinc Processing 158

60 Fugitive Emission Factors for Primary Slab Zinc Processing 159

61 Total Particulate Emission Factor Data and Estimates -- Primary Slab Zinc Processing 163

62 Particulate Emissions Trace Metal Content 164

63 Particulate Emissions Chemical Composition for Uncontrolled Roasting Emissions 164

TABLES (Continued)

Number		Page
7.1-1	Raw Material and Energy Requirements for Aluminum Production	169
7.1-2	Emission Factors for Primary Aluminum Production Processes	171
7.1-3	Uncontrolled Emission Factors and Particle Size Distribution for Roof Monitor Fugitive Emissions from Prebake Aluminum Cells	172
7.1-4	Uncontrolled Emission Factors and Particle Size Distribution for Roof Monitor Fugitive Emissions from HSS Aluminum Cells	173
7.1-5	Uncontrolled Emission Factors and Particle Size Distribution for Primary Emissions from HSS Reduction Cells	174
7.3-1	Typical Sulfur Dioxide Concentration in Offgases.	183
7.3-2	Emission Factors for Primary Copper Smelters.	184
7.3-3	Particle Size Distribution and Size Specific Emission Factors for Multiple Hearth Roaster and Reverberatory Smelter Operation	185
7.3-4	Particle Size Distribution and Size Specific Emission Factors for Reverberatory Smelter Operation	186
7.3-5	Particle Size Distribution and Size Specific Emission Factors for Copper Converter Operations	187
7.3-6	Fugitive Emission Factors for Primary Copper Smelters	188
7.3-7	Uncontrolled Particle Size and Size Specific Emission Factors for Fugitive Emissions from Reverberatory Furnace Matte Tapping Operations.	189
7.3-8	Particle Size Distribution and Size Specific Emission Factors for Fugitive Emissions from Reverberatory Furnace Slag Tapping Operations.	190
7.3-9	Particle Size Distribution and Size Specific Emission Factors for Fugitive Emissions from Converter Slag and Copper Blow Operations.	191

TABLES (Concluded)

Number Page

7.3-10 Lead Emission Factors for Primary Copper Smelters 192

7.6-1 Uncontrolled Emission Factors for Lead Smelting 201

7.6-2 Lead Emission Factors and Particle Size Distribution for Baghouse Controlled Blast Furnace Flue Gases. 203

7.6-3 Uncontrolled Fugitive Emission Factors and Particle Size Distribution for Lead Ore Storage 204

7.6-4 Uncontrolled Lead Fugitive Emission Factors and Particle Size Distribution for Sinter Machine 205

7.6-5 Uncontrolled Lead Fugitive Emission Factors and Particle Size Distribution for Blast Furnace. 206

7.6-6 Uncontrolled Lead Fugitive Emission Factors and Particle Size Distribution for Dross Kettle 207

7.6-7 Uncontrolled Lead Fugitive Emission Factors and Particle Size Distribution for Reverberatory Furnace. 208

7.6-8 Uncontrolled Fugitive Emission Factors for Primary Lead Smelting Processes. 209

7.6-9 Typical Control Device Efficiencies in Primary Lead Smelting Operations. 210

7.11-1 Emission Factors for Secondary Lead Processing. 216

7.11-2 Fugitive Emission Factors for Secondary Lead Processing . . . 217

7.11-3 Emission Factors and Particle Size Distribution for Baghouse Controlled Blast Furnace Flue Gases 218

7.11-4 Emission Factors and Particle Size Distribution for Uncontrolled and Baghouse Controlled Blast Furnace Ventilator. . . 219

7.11-5 Efficiency of Particle Control Equipment Associated with Secondary Lead Smelting Furnaces. 220

7.7-1 Particulate Emission Factors for Primary Slab Zinc Processing 229

7.7-2 Uncontrolled Fugitive Particulate Emission Factors for Primary Slab Zinc Processing. 230

SECTION 1

INTRODUCTION

There is increasing interest in the presence of fine particulate in the atmosphere and how existing technology is controlling fine particulate emissions. Fine particulate emissions (i.e., particles smaller than 20 microns (μm) in size) are of interest since being demonstrated to be of respirable size. The physiological response to inhalation of fine particulate differs widely, however, depending on chemical composition.

This document is a source category report on inhalable particulate emitted by the nonferrous industry, specifically:

- Primary aluminum production
- Primary copper smelting
- Primary lead smelting
- Secondary lead processing
- Primary zinc smelting

This report summarizes available inhalable particulate emissions data from typical sources of each industry. The primary objective is to report reliable total and size-specific emission factors for controlled and uncontrolled emissions for each emission source in each of the nonferrous industries.

The second objective of this report is to summarize existing data on chemical characterization of inhalable particulate emissions from each emission source in each of the five nonferrous industries studied.

The final objective of this report is to present an update for the appropriate section in the document "Compilation of Air Pollutant Emission Factors" (AP-42) which is revised periodically. Section 7.1 "Primary Aluminum Production" was last revised in April 1981; Section 7.3 "Primary Copper Smelting" in January 1984. Section 7.6 "Primary Lead Smelting" was last revised in February 1980, whereas Section 7.7 "Primary Zinc Smelting" has not been revised since February 1972. Section 7.11 "Secondary Lead Processing" was last revised in October 1980. None of the sections, however, currently contain data on fine particulate emissions. (Ref. 1)

The above objectives were met by an intensive literature search and contacts with individuals and organizations known to be familiar with the nonferrous metal industries. Sources of information included:

- DIALOG computerized literature searches
- Control agencies
  - U.S. Environmental Protection Agency
  - State and local air pollution control agencies
- Trade organizations
  - Aluminum Association
  - Copper Development Association
  - International Lead Zinc Research Organization
- Industry contacts
- AP-42 nonferrous industries files at the Office of Air Quality Planning and Standards (OAQPS)
- Fine Particle Emission Information System (FPEIS)

Particle sizes are usually expressed in terms of the equivalent aerodynamic diameter; i.e., the diameter of a sphere of unit density that reaches the same terminal settling velocity (at low particle Reynolds number in still air) as the actual particle. This method of size expression is useful because it is readily determined through straightforward measurement; where the other properties of actual particle size and density may not be obtainable.

There are two general classifications of particle size measurement systems, 1) inertial separation and 2) optical or electrical mobility measurement. The majority of all particle sizing currently performed in source testing uses equipment based on inertial separation. Inertial impactors are designed so that each plate in the impactor collects particles of one size range expressed as d_{50}, the particle size in microns for which 50 percent of the particles are theoretically collected on the particular sampling plate or stage. When data are analyzed, it is convenient to express the results as a cumulative percentage by weight at selected equivalent aerodynamic diameters or cut points to facilitate analysis.

The data were reviewed, analyzed, and ranked according to the criteria provided in the report "Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections" April 1980 . If there were no reason to exclude particular data from consideration, each data set was assigned a ranking. The data were ranked as follows:

A -- Tests performed by a sound methodology and reported in enough detail for adequate validation. These tests are not necessarily EPA reference method tests, although such reference methods are certainly to be used as a guide.

B -- Tests performed by a generally sound methodology but lacking enough detail for adequate validation.

C -- Tests based on an untested or new methodology or lacking a significant amount of background data.

D -- Tests based on a generally unacceptable method but that may provide an order-of-magnitude value for the source.

Upon ranking the data, size-specific emission factors were calculated rather than a range of values for each cut point.

The calculation of the size-specific emission factors was performed in two ways. In the first method, sufficient process and mass emission data were available to calculate cumulative factors directly. These factors are calculated by applying the cumulative percentage for each cut point to the mass emission factor calculated from production data for that test. The size-specific emission factors are subsequently graphed versus particle size and, from the resulting curve, the cumulative emissions factors are determined for equivalent aerodynamic particle diameters of 15, 10, 5, 2.5, 1.25, and 0.625 μm.

Example of Method 1:

- Industry: Primary aluminum
- Source: Horizontal stud Soderberg reduction cell
- Emissions: Fugitive roof monitor
- Particle size distribution (measured)

Run		Particle size mass distribution					
1	d_{50} (μm)	15.78	6.30	3.02	1.65	1.20	0.53
	Cum. % <d_{50}	39.8	23.1	17.1	14.3	11.6	7.3
2	d_{50} (μm)	15.7	6.72	2.94	1.57	1.12	0.46
	Cum. % <d_{50}	39.8	23.1	17.1	14.3	11.6	7.3

When graphed, the following average cut points can be read:

- Mean particle size distribution

Cut point (μm)	15	10	5	2.5	1.25	0.625
Mean cumulative percentage less than cut point	35.5	31.0	25.0	17.5	12.5	8.5

- Mass emission rate: 7.2 lb/ton of aluminum (calculated using EPA Method 5 total, particulate loading plus process data)

- Size-specific emission factors (EF)*

$$EF_{15\ \mu m} = \text{Mass emission factor} \times \frac{\text{Mean cumulative percentage less than 15 } \mu m}{100}$$

$$= 7.20 \text{ lb/ton} \times 35.5/100$$

$$= 2.56 \text{ lb/ton}$$

Similarly:

$EF_{10\ \mu m}$ = 2.23 lb/ton

$EF_{6\ \mu m}$ = 1.80 lb/ton

$EF_{2.5\ \mu m}$ = 1.26 lb/ton

$EF_{1.25\ \mu m}$ = 0.86 lb/ton

$EF_{0.625\ \mu m}$ = 0.61 lb/ton

The second method involved the use of the mass emission factors found in AP-42. Emission factors can be calculated by applying the mean cumulative percentages for each cut point to the mass emission factor presented in AP-42. This is the preferred method since AP-42 mass emission factors are generally based on several samples taken at multiple points in ducting rather than single points typical of particle distribution sampling.

---

*To convert to kilograms per metric ton (kg/Mg), multiply by 0.5.

Example of Method 2:

- Industry: Primary aluminum
- Source: Prebake cell
- Emissions: Fugitive roof monitor
- Particle size distribution (measured)

Run		Particle size distribution					
1	d_{50} (μm)	16.74	6.86	2.46	1.30	0.71	0.36
	Cum. % $<d_{50}$	53.4	34.8	19.11	15.5	11.1	8.3
2	d_{50} (μm)	16.70	6.83	2.45	1.30	0.71	0.35
	Cum. % $<d_{50}$	58.9	38.9	21.4	16.7	13.5	9.9
3	d_{50} (μm)	16.8	6.90	2.47	1.31	0.72	0.36
	Cum. % $<d_{50}$	97.4	67.3	33.5	28.6	22.5	16.2

When graphed, the following average cut points can be read:

- Mean particle size distribution

Cut point (μm)	15	10	5	2.5	1.25	1.00	0.625
Mean cumulative percentage less than cut point	68.0	58.5	45.0	26.5	20.0	18.3	15.5

- Mass emission factor from AP-42: 5 lb/ton of aluminum
- Assumption: During the tests, the fugitive emissions from the prebake cells were approximately equal to the mass emission factor from AP-42
- Size-specific emission factors (EF)*

---

*To convert to kilograms per metric ton (kg/Mg), multiply by 0.5.

$$EF_{15\ \mu m} = \text{mass emission factor} \times \frac{\text{Mean cumulative percentage less than 15 } \mu m}{100}$$

$$= 5\ \text{lb/ton} \times 68/100$$

$$= 3.4\ \text{lb/ton}$$

Similarly:

$EF_{10\ \mu m} = 2.9$ lb/ton

$EF_{5\ \mu m} = 2.2$ lb/ton

$EF_{2.5\ \mu m} = 1.3$ lb/ton

$EF_{1.25\ \mu m} = 1.0$ lb/ton

$EF_{1.00\ \mu m} = 0.9$ lb/ton

$EF_{0.625\ \mu m} = 0.8$ lb/ton

The reliability of the calculated emission factors is indicated by an Emission Factor Rating. The ratings are subjective quality evaluations rather than statistical confidence intervals and range from A (excellent) to E (poor) as follows:

A -- Excellent. Developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category* is specific enough to minimize variability within the source category population.

B -- Above average. Developed only from A-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As in the A rating, the source category is specific enough to minimize variability within the source category population.

C -- Average. Developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As in the A rating, the source category is specific enough to minimize variability within the source category population.

D -- Below average. The emission factor was developed only from A-and B-rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are footnoted in the emission factor table.

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*Source category: A category in the emission factor table for which an emission factor has been calculated; generally a single process.

E -- Poor. The emission factor was developed from C-and D-rated test data, and there may be reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are always footnoted.

Process and control system operating data were obtained and summarized. Cyclic or other peculiarities which may affect emissions were identified and presented in both the specific industry description sections and in the proposed AP-42 sections. Because of the nature of AP-42, some duplication of information occurs in the proposed AP-42 sections and in the industry descriptions.

SECTION 2

PRIMARY ALUMINUM INDUSTRY

This section presents the source category report on inhalable particulate matter emissions from processes within the primary aluminum industry. The industry includes the production of alumina from bauxite and the reduction of alumina to aluminum. Size-specific emission factors are developed from data obtained from particulate sampling tests performed on industrial emission sources. A proposed revision of the AP-42 section for this industry is also presented.

Included in this section are brief descriptions of the aluminum industry including a process flow diagram, the individual processes involved in aluminum production, sources of particulate emissions, and types of control equipment used.

2.1 OVERVIEW

Primary aluminum production is a two-step process involving the production of alumina (Al_2O_3) from bauxite, known as the Bayer Process, and the electrolytic reduction of the alumina to produce aluminum, the Hall-Heroult Process. These two steps are normally carried out at different locations.

Ten domestic firms in the United States currently produce primary aluminum. These are summarized in Table 1. In 1982, 12 domestic firms, owned by 11 companies, were involved in the production of primary aluminum in the United States. Of the domestic firms, only Alcoa and Reynolds were integrated from domestic mines through the primary metal stage (Ref. 2). Figure 1 shows the breakdown of U.S. primary aluminum raw material supply and production as of 1981.

For many years, demand for aluminum had grown at a faster rate than for other metals. Total U.S. industrial demand increased from 4,792 thousand tons (4,347 thousand Mg) in 1972 to an estimated 5,749 thousand tons (5,215 thousand Mg) in 1981, although demand in 1973, 1974, 1977, 1978, and 1979 exceeded 6,200 thousand tons (5,625 thousand Mg). Measured either in quantity or value, the use of aluminum now exceeds all other metals except iron. U.S. demand for aluminum in metal and nonmetal forms is expected to be 8 to 17 million tons (7.3 to 15.4 million Mg) by the year 2000. Principal factors contributing to the high demand forecast include increased use of aluminum in the transportation sector and in a wide variety of both consumer

TABLE 1. PRIMARY ALUMINUM PRODUCERS IN THE UNITED STATES 1984[a]

ALUMAX, Inc.
Owned by AMAX, Inc., MITUSI &
Co., Ltd., and NIPPON Steel
Corp.
400 S. El Camino Real
San Mateo, CA 94402

Aluminum Company of America (ALCOA)
1501 Alcoa Building
425 Sixth Avennue
Pittsburgh, PA 15219

Anco Metals Co. (previously known as
The Anaconda Company)
Subsidiary of Atlantic Richfield Co.
Aluminum Division
2 Continental Tower
1701 Golf Road
Rolling Meadows, IL 60008

Consolidated Aluminum Corp. (CONALCO)
Owned by Swiss Aluminum Corp.
and Phelps Dodge Corp.
11960 Westline Industrial Dr.
St. Louis, MO 63178

Kaiser Aluminum & Chemical Corp.
300 Lakeside Drive
Oakland, CA 94612

Martin Marietta Aluminum, Inc.
Subsidiary of Martin
Marietta Corp.
6801 Rockledge Drive
Bethesda, MD 20034

National Southwire
Owned by National Intergroup Corp.
2800 Grant Building
310 Grant Street
Pittsburgh, PA 15219
and
Southwire Co.
Fertilla Street
Carrollton, GA 30117

Noranda Aluminum, Inc.
Subsidiary of Noranda Mines, Ltd.
P.O. Box 70
St. Jude Industrial Park
New Madrid, MO 63869

Ormet Corp.
Consolidated Aluminum Corp.
11960 Westline Industrial Drive
St. Louis, MO 63178

Reynolds Metals Co.
P.O. Box 27003
Reynolds Metals Building
6601 W. Broad Street
Richmond, VA 23261

[a] Source: The Aluminum Association.

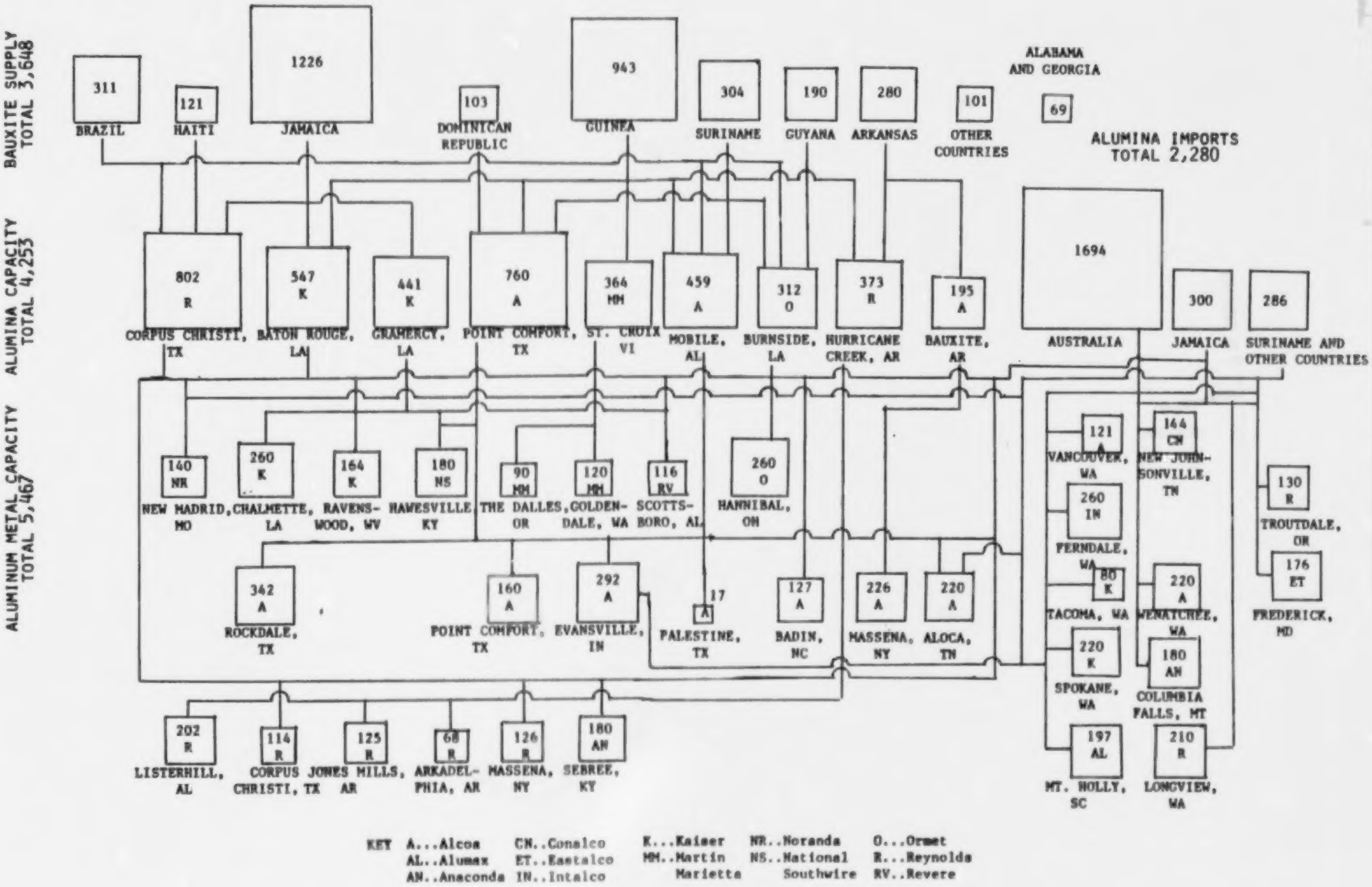
BAUXITE SUPPLY TOTAL 3,648
ALUMINA CAPACITY TOTAL 4,253
ALUMINUM METAL CAPACITY TOTAL 5,467
311 BRAZIL
121 HAITI
1226 JAMAICA
103 DOMINICAN REPUBLIC
943 GUINEA
304 SURINAME
190 GUYANA
280 ARKANSAS
101 OTHER COUNTRIES
ALABAMA AND GEORGIA 69
ALUMINA IMPORTS TOTAL 2,280
802 R CORPUS CHRISTI, TX
547 K BATON ROUGE, LA
441 K GRAMERCY, LA
760 A POINT COMFORT, TX
364 MM ST. CROIX VI
459 A MOBILE, AL
312 O BURNSIDE, LA
373 R HURRICANE CREEK, AR
195 A BAUXITE, AR
1694 AUSTRALIA
300 JAMAICA
286 SURINAME AND OTHER COUNTRIES
140 NR NEW MADRID, MO
260 K CHALMETTE, LA
164 K RAVENSWOOD, WV
180 NS HAWESVILLE KY
90 MM THE DALLES, OR
120 MM GOLDENDALE, WA
116 RV SCOTTSBORO, AL
260 O HANNIBAL, OH
121 A VANCOUVER, WA
164 CN NEW JOHNSONVILLE, TN
260 IN FERNDALE, WA
130 R TROUTDALE, OR
342 A ROCKDALE, TX
160 A POINT COMFORT, TX
292 A EVANSVILLE, IN
17 A PALESTINE, TX
127 A BADIN, NC
226 A MASSENA, NY
220 A ALOCA, TN
80 K TACOMA, WA
220 A WENATCHEE, WA
176 ET FREDERICK, MD
220 K SPOKANE, WA
180 AN COLUMBIA FALLS, MT
202 R LISTERHILL, AL
114 R CORPUS CHRISTI, TX
125 R JONES MILLS, AR
68 R ARKADELPHIA, AR
126 R MASSENA, NY
180 AN SEBREE, KY
197 AL MT. HOLLY, SC
210 R LONGVIEW, WA
KEY
A...Alcoa
AL..Alumax
AN..Anaconda
CN..Conalco
ET..Eastalco
IN..Intalco
K...Kaiser
MM..Martin Marietta
NR..Noranda
NS..National Southwire
O...Ormet
R...Reynolds
RV..Revere

Figure 1. Distribution of U.S. bauxite and alumina supply and aluminum plant capacities, 1981 (thousand short tons aluminum equivalent) (Ref. 3).

and capital goods. In the long term, the availability and anticipated low cost of aluminum, relative to competing materials such as copper and plastics, could also contribute to attainment of the high demand forecast. Factors that could result in a lower use forecast are possible low growth, the high cost of electric energy, and the substitution of other materials for aluminum in transportation, machinery, construction, containers, and electrical distribution lines.

The aluminum industry itself has contributed greatly to the growth in aluminum demand by maintaining a large research effort to develop new products and improve production efficiency. Current research covers the entire field of metal production through the development of new and improved production processes, alloys and casting techniques, protective and decorative finishes, end-use applications, and recycling processes. Research is also being conducted to improve the energy efficiency of the aluminum production process. These efforts include reducing heat losses, regenerative heating, and increasing the product yield in the Bayer process; and reducing the electrical resistance of the anode, cathode, and electrolyte, which wastes much of the power input as heat, in the Hall-Heroult process (Ref. 2 and 3).

2.1.1 Aluminum Production Process

The following section describes the production of primary aluminum, which involves a two-step process as indicated in the aluminum production process flow diagram (Figure 2).

The first step in the aluminum production process consists of alumina extraction from the base ore, normally bauxite, although the use of kaolin, anorthosite, and alumite clays is anticipated in the future. Although research on alumina extraction from all ores is continuing, virtually all of the commercially produced alumina is extracted from bauxite by the Bayer process.

In the Bayer process, the ore is dried, ground in ball mills, then leached with a caustic solution at an elevated temperature and pressure, producing a sodium aluminate solution which is separated and cooled. As the solution cools aluminum precipitates as hydrated aluminum oxide ($Al_2O_3 \cdot 3H_2O$). The resulting Al_2O_3 is then transported to primary aluminum reduction facilities. With the exception of the Alcoa facility at Point Comfort, Texas, alumina production and reduction are accomplished at separate locations (Ref. 2).

Primary aluminum is produced by the electrolysis of alumina in a molten bath of natural or synthetic cryolite (Na_3AlF_6) which serves as both an electrolyte and a solvent for the Al_2O_3. The reduction is carried out in shallow rectangular cells called pots, that are made of carbon-lined steel and include carbon blocks that are suspended above and extend down into the pots (see Figure 3). The pots and carbon blocks serve as cathodes and anodes, respectively, for the electrolytical process. Resistance between the electrodes heats the alumina-cryolite bath to between 1,700° and 1,800°F

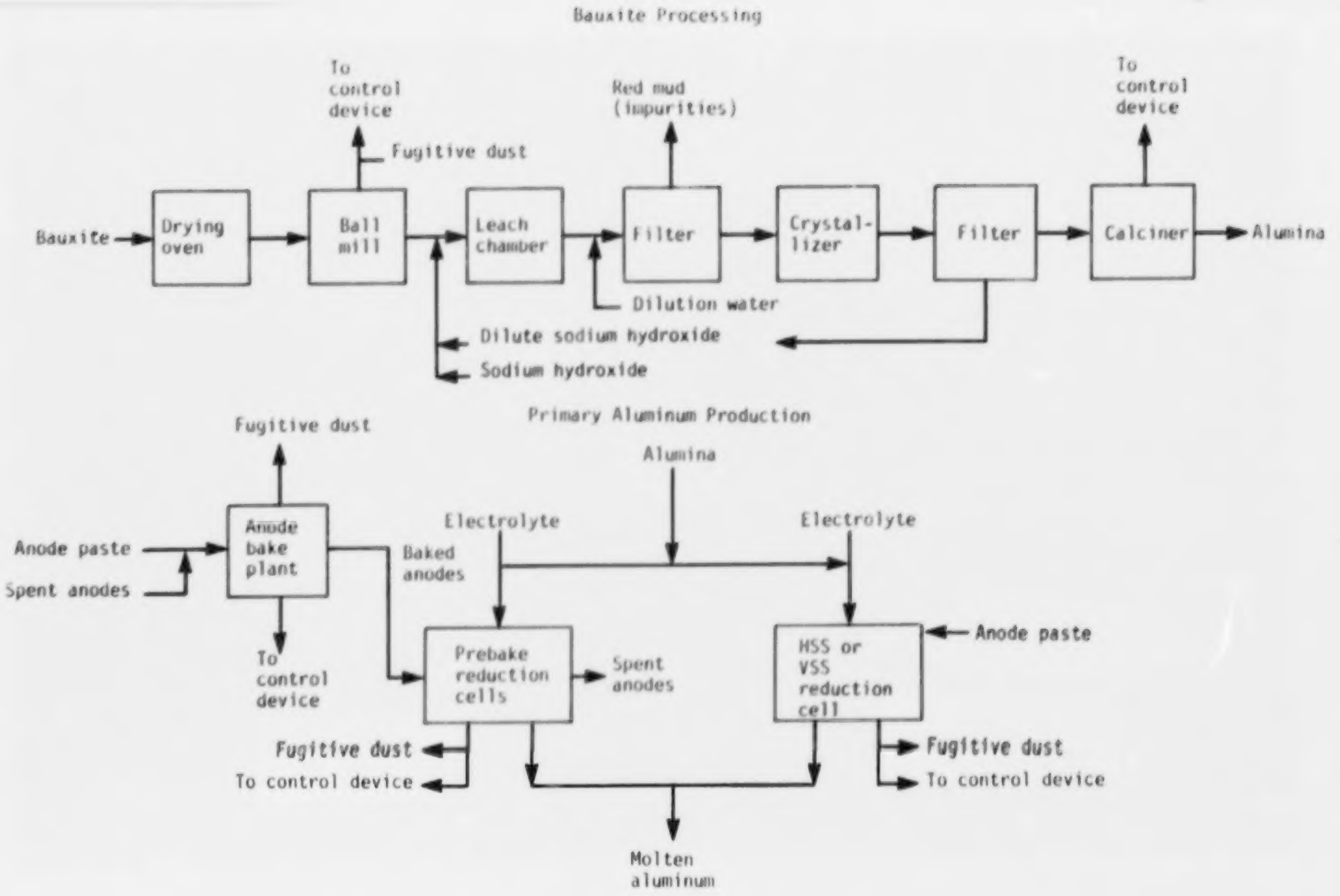
Bauxite Processing
Bauxite
Drying oven
Ball mill
To control device
Fugitive dust
Leach chamber
Filter
Red mud (impurities)
Dilution water
Dilute sodium hydroxide
Sodium hydroxide
Crystal-lizer
Filter
Calciner
To control device
Alumina
Primary Aluminum Production
Fugitive dust
Anode paste
Spent anodes
Anode bake plant
To control device
Baked anodes
Electrolyte
Alumina
Electrolyte
Prebake reduction cells
Spent anodes
Fugitive dust
To control device
HSS or VSS reduction cell
Anode paste
Fugitive dust
To control device
Molten aluminum

Figure 2. Aluminum production process flow diagram.

TYPING GUIDE SHEET

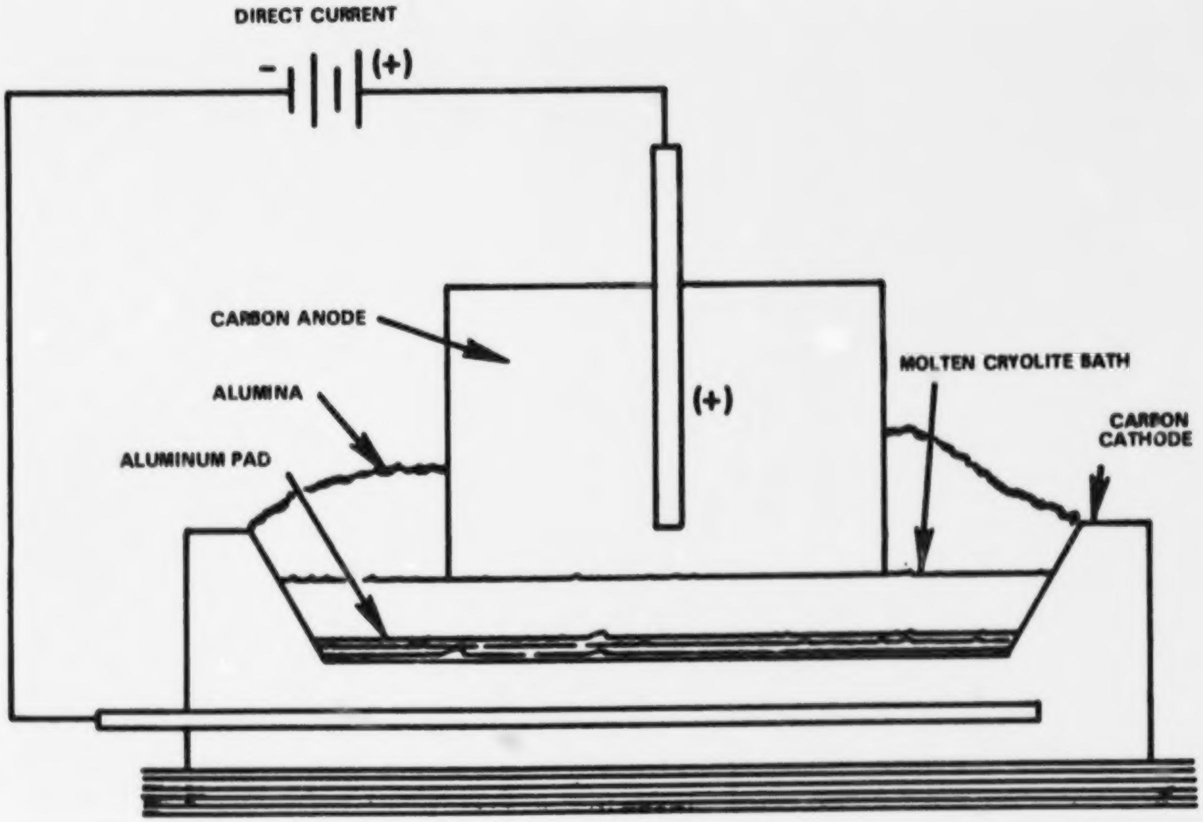
DIRECT CURRENT
-
(+)
CARBON ANODE
(+)
ALUMINA
ALUMINUM PAD
MOLTEN CRYOLITE BATH
CARBON CATHODE

Figure 3. Aluminum reduction cell diagram (Ref. 4).

(925° and 980°C), causing the alumina to dissociate. The aluminum has a higher density than the bath and settles at the cathode.

Al_2O_3 and Na_3AlF_6 are periodically added to the bath to replenish material that is removed or consumed during normal operation. The weight ratio of sodium fluoride (NaF) to aluminum fluoride (AlF_3) in Na_3AlF_6 is 1:50. However it has been found that adding excess AlF_3 to reduce the bath ratio from 1:30 to 1:45 will increase cell current efficiency and lower the bath melting point permitting lower operating temperatures and lower energy consumption per pound of aluminum produced. Calcium fluoride (CaF_2) may also be added to lower the bath temperature (Ref. 2 and 4).

Every 1 or 2 days, the molten aluminum is removed from the bottom of the pot by a vacuum siphon technique. Steel crucibles lined with refractory with or without airtight lids and downward-sloping spouts are used to withdraw the molten metal. As the cast iron pot is evacuated, the molten aluminum is drawn into the crucible, but only a portion of the molten aluminum is removed. The molten metal is then blended in a holding furnace with other batches of metal and may be fluxed, alloyed, and cast into various solid forms, or transported in the molten state to fabricating plants (Ref. 2).

Pots are connected in electrical series ranging from 100 to 240 cells to form a potline, the basic production unit of the reduction plant. The cells utilize direct current ranging from 60,000 to 280,000 amps, with the majority of plants having 80,000 to 100,000 amps cells. Typical anode current densities range from 600 to 800 amp/ft^2 (6.5 to 8.6 kA/m^2), but may be substantially greater than 800 amp/ft^2 (8.6 KA/m^2). The voltage drop across a single cell is 4.0 to 5.2 volts, and across an entire potline may run as high as 1,000 volts.

Larger cells require less manpower per pound of aluminum produced; however, special problems are encountered in cells designed to use 100,000 or more amperes as powerful magnetic fields are created in the metal and bath, resulting in violent agitation. The agitation disperses the aluminum in the bath, increasing the possibility of reversing the reduction reaction. Also, the molten metal piles up toward the anode leads, causing a variation in the anode-cathode spacing. The magnetic fields may also produce localized thermal effects which can distort the carbon lining in the pots. Through experience, the industry has learned how to balance the magnetic fields to minimize these problems.

Current efficiency ranges from 85 to 90 percent with losses caused by metal spillage, vaporization from the bath, and reoxidation of aluminum. Because of electrical resistance, the voltage efficiency is only 40 percent, with heat being lost by radiation, exhaust gases, tapped metal, and electrodes removed from the cell. As a result, the overall energy efficiency is about 35 percent (Ref. 2).

The dissociation of Al_2O_3 liberates oxygen (O_2) from the bath, which consumes the anode, producing carbon monoxide (CO) and carbon dioxide (CO_2) continually. The method of anode replacement is the only significant variation among primary production facilities within the United States, with two standard methods in use, the prebake process and the Soderberg continuous process.

Prebake Process

As the name implies, the prebake aluminum reduction process uses prebaked carbon blocks as anodes. The carbon blocks are produced as an ancillary operation at the reduction plant site using a process similar to the schematic shown in Figure 4. In the anode production plant, coke is crushed, sized, cleaned, and mixed with the crushed remains of spent anodes. This mixture is then blended with pitch and molded to form self-supporting green anode blocks. The pitch may or may not be coal tar as depicted in the figure and it may be received in a molten state and handled as a liquid. The green anode blocks are then baked in a ring furnace or tunnel kiln.

A ring furnace consists of compartmentalized, sunken brick baking pits with surrounding interconnecting flues. Green anodes are packed within the pits, with all empty space around the blocks filled with a blanket of coke or anthracite. A blanket of calcined petroleum coke covers the top of each pit. The packing and cover help to prevent oxidation of the carbon anodes.

The pits are then fired with manifold burners using either natural gas or oil. The flue system is designed so hot gas being fired into the pits is drawn through the next batch of anodes to preheat them gradually. Also, by incorporating flues on the outside walls, which operate under draft, and pit walls of dry-type construction, the flue system draws most volatile materials (principally hydrocarbons from the pitch binder) along with the burner combustion products into the flue gases, where they are burned at about 2,370°F (1,300°C). Combustion air is drawn through the previously fired sections, thereby cooling them. The anodes are fired to approximately 2,190°F (1,200°C), and the cycle of placing the green anodes, preheating, firing, cooling, and removal takes approximately 28 days (Ref. 4).

Firing of sections proceeds down one side of the rectangular furnace building and back up the other in a ring pattern. The pattern of cooling, firing, heating, and emptying sections is repeated continually, moving from section to section. The baked anodes are stripped from the furnace pits by an overhead crane on which pneumatic systems for loading and removing the coke pit packing may also be mounted. The packing may subsequently become part of other green anodes in the carbon plant (Ref. 4).

A second type of furnace, the tunnel kiln, has been developed for application in the baking of anodes. The kiln is an indirect-fired chamber in which a controlled atmosphere is maintained to prevent oxidation of the carbon anodes. Green anode blocks are loaded on transporter units that enter the kiln through an air lock, pass successively through a preheating zone, firing zone, and cooling zone, and leave the kiln through a second air lock. The refractory beds of the cars are mechanically sealed to the kiln walls to form the muffle chamber, and still permit movement of the units through the

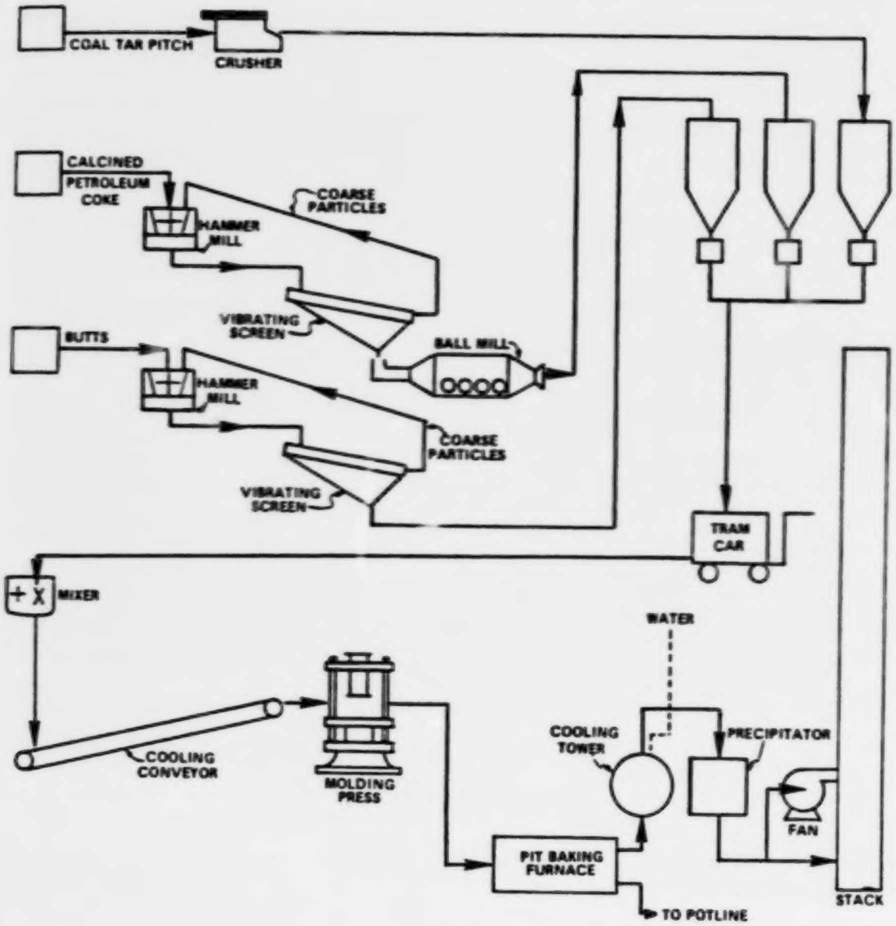
COAL TAR PITCH
CRUSHER
CALCINED
PETROLEUM
COKE
HAMMER
MILL
COARSE
PARTICLES
VIBRATING
SCREEN
BALL MILL
BUTTS
HAMMER
MILL
COARSE
PARTICLES
VIBRATING
SCREEN
TRAM
CAR
MIXER
WATER
COOLING
TOWER
PRECIPITATOR
COOLING
CONVEYOR
MOLDING
PRESS
FAN
PIT BAKING
FURNACE
STACK
TO POTLINE

Figure 4. Flow diagram for preparation of prebake anodes (Ref. 5).

kiln. The muffle chamber is externally heated by combustion gases, and the products of combustion are discharged through an independent stack system.

Effluent gases from the baking anodes may be introduced into the fire box to recover the fuel value of hydrocarbons and reduce the quantity of unburned hydrocarbon to approximately 1 percent of that coming from a ring furnace.

Although the tunnel kiln presents mechanical problems in design and operation, it is reported to have several appreciable advantages over the ring-type furnace:

- Baking cycle from green to finished anode is much shorter
- Anode baking is more uniform
- Space requirements for equal capacity furnaces is less
- Smaller gas volumes are handled through the furnace emission control system

The development of the tunnel kiln in this application is recent, and there is only one installation that presently has this technology available and it may not be in operation. Most experts do not view the tunnel kiln as an acceptable alternative for baking carbon.

Baked anodes, from either type of bake plant, are delivered to air blast cleaning machines utilizing fine coke as blasting grit. Fins, scrafs, and adherent packing is removed by this treatment, and the baked anodes are then transferred to the rodding room where the electrodes are attached (Ref. 4).

Prebake Cell

Prebake cells use up to 28 anode assemblies per cell, which are attached to the anode bus on the cell superstructure by clamps. The anode bus is attached to the steel superstructure by anode jacks that may be driven by an air motor or other means, giving a travel distance ranging from 10 to 14 in. (25 to 36 cm) and permitting the raising or lowering of all 26 assemblies in the cell simultaneously. Each of the 28 assemblies may also be raised or lowered individually by means of an overhead crane after the anode clamp is loosened.

The anodes are lowered as they are consumed, typically at a rate of about 1 in. (2.5 cm) per day (Ref. 6). When the anodes are completely spent, they are removed and replaced on a rotating basis, usually a pair at a time. The total operating time before replacement is dependent on the size of the anode blocks and the amperage of the potline.

The anode assemblies are usually installed in two rows extending the length of the cell. In some arrangements the two rows are closely spaced in the center of the cell, providing a working area on each side of the cell between the cell side lining and the anodes (side-worked). In other cases, the rows are separated and placed closer to the cell side lining, providing the working area in the center of the cell between the rows of anodes (center-worked).

The general trend in prebake anode design has been toward larger anode blocks, obtaining greater effective anode/cathode surface ratios and lower current densities at the anodes for equivalent power inputs.

Soderberg Cells

There are two types of Soderberg cells -- vertical stud Soderberg (VSS) and horizontal stud Soderberg (HSS). Each is a single large carbon anode, but they differ in the method of anode bus connection to the anode mass. In both the VSS and HSS a green anode paste is fed periodically into the open top of a rectangular steel compartment and baked by the heat of the cell to a solid coherent mass as the material moves down the casing.

In both types of Soderberg cells, the in-place baking of the anode paste results in the release of hydrocarbon fumes and volatiles derived from the pitch binder of the paste mixture. These products are a component of the Soderberg cell emissions and are essentially absent from those of the prebake cells.

Soderberg cells were acclaimed initially because they eliminated the need for a separate anode manufacturing facility. Because prebake cells can be built in much larger units than Soderberg cells, volatile pitch components can condense in the ductwork and control device; and because simultaneously controlling fluorides and organic emissions can be a problem, any economic advantage the Soderberg systems once had is diminishing. The trend appears to be toward the use of the prebake cell.

Furthermore, although prebake cells may be center-worked or side-worked, the use of a single large carbon anode requires that both types of Soderberg cells be side-worked. Center-worked cells lend themselves to more efficient hooding and hence more efficient emission control.

Vertical Stud Cells

For a typical vertical stud Soderberg (VSS) reduction cell, the anode casing is stationary, the electrical connection from the studs to the busbar is rigid, and the steel current-carrying studs project vertically through the unbaked paste portion into the baked portion of the anode. As the anode is consumed and moves down the casing, the bottom-most studs are periodically extracted before they become exposed to the bath at the bottom of the anode.

The stationary anode casing and the projection of the studs through the top of the anode allow the installation of a gas collection skirt between the anode casing and the bath surface. The gases are ducted to integral gas burners where the hydrocarbon tars are burned to gaseous fractions that do not interfere with the operation of subsequent pollutant removal equipment. Maintenance of the skirt system is a problem, however. Irregularities in cell operation can extinguish the burner flame, and the skirts may melt or be deformed by the heat. Pilot lights can help ensure that the burners stay lit.

Horizontal Stud Cells

For a typical horizontal stud Soderberg (HSS) reduction cell, the anode, suspended over the pot, is contained in a rectangular compartment made of aluminum sheeting and perforated steel channels that is raised or lowered by powered jacks. The entire anode assembly is moved downward as the working surface is oxidized. Studs are inserted into the anode through perforations in the steel channels at a point approximately 3 ft (0.9m) above the molten bath where the paste is still fairly soft. Electrical contact is made through flexible connectors between the studs and the busbar. As the anode is moved downward, the paste becomes solid as it bakes and grips the stud. When the bottom channel reaches the bath, the flexible connectors are moved to a higher row of studs, the studs in the bottom row are pulled out, and the bottom channels are removed.

The construction of the HSS cell prevents the installation of an integral gas collection device such as a skirt, since the anode casing is formed by removable channels supporting the horizontal stud electrodes, and these channels are periodically changed as the anode moves downward and is consumed. Hooding is restricted to canopy suspension, resulting in so much air dilution that self-supporting combustion in burners is not possible. Therefore, the hydrocarbon tars condense in the ductwork and tend to plug pollutant removal equipment.

2.1.2 Particulate Emission Sources

Sources of particulate emissions within the primary aluminum industry are shown schematically in Figure 2. At the alumina production plant, bauxite is ground and digested to produce sodium aluminate. The major source of emissions during this operation is the ore grinder. After precipitation, the $Al_2O_3 \cdot 3H_2O$ is calcined in a rotary kiln to produce Al_2O_3. The kiln is usually equipped with a particulate collection device to recover the alumina dust for economic reasons.

At the aluminum reduction plant, Al_2O_3 is reduced to aluminum in an electrolytic cell. This operation produces particulate, sulfur, carbon monoxide, and hydrocarbon emissions as well as fluoride emissions. The amount of emissions depends upon the type of cell used.

Prebake Cells

The electrolytic reduction of aluminum produces a CO exhaust at the anode of the cell. As the exhaust leaves the cell, it entrains particulates including fluoride salts. This exhaust also contains noxious gases such as hydrogen fluoride (HF), sulfur dioxide (SO_2), and traces of hydrogen sulfide (H_2S).

In a prebake plant the carbon anode, which is consumed as part of the reaction, is formed in a baking furnace. The manufacturing process is similar to coke-making in that a paste made of pitch and calcined petroleum coke is devolatilized forming a solid carbon anode. The process emits large amounts of hydrocarbons, sulfur compounds, and particulates.

Soderberg Cells

Plants which use Soderberg cells do not require anode furnaces because the anode is formed from a coke-based paste within the electrolytic cell itself. In this case, the particulate, sulfur dioxide, hydrogen sulfide, and hydrocarbon emissions common to the anode furnace of a prebake cell will be emitted in the electrolytic cell of the Soderberg process instead.

As has been discussed, there are two types of Soderberg cells: HSS and VSS. With respect to air pollution control, the primary difference between these two is the ease with which a hood can be placed over a cell to capture emissions. In HSS cells, the hood does not fit close to the pot and large volumes of air are entrained with the hot exhaust from the cell. This has the effect of quenching the combustion of hydrocarbons, resulting in a tar fouling problem as the heavy hydrocarbons condense on ducts and control equipment (Ref. 7).

2.1.3 Particulate Emission Controls

The Bayer plant has only two sources of particulate emissions to control as follows:

- Particulate matter from the ore grinder is normally collected in a hood and removed using a high efficiency electrostatic precipitator (ESP), venturi scrubber, or bag filter. Low efficiency wet collection devices such as spray towers, floating bed scrubbers, quench towers, and spray screens have been used in the past, but are generally not effective enough to comply with current standards and probably have been replaced.

- Particulate matter from the rotary kiln calcining operation is removed using a combination of multicyclone followed by ESP or bag filter. Because of the economic value of the collected alumina dust, low efficiency devices that have been used have probably all been replaced.

The electrolytic reduction process requires controls for particulate matter, fluorides, sulfur dioxide (SO_2), and hydrocarbons. The control technology applied depends upon the type of electrolytic cell being used. Table 2 contains a summary of the pertinent emission characteristics of the three cell types. Most control systems rely primarily upon a dry alumina scrubber to remove particulate matter and gaseous HF acid. However, many of the plants with the older control systems (i.e., other than dry alumina scrubbers) have closed down due to economic reasons and probably will not be restarted. Note, however, the following specific emission control requirements:

- Prebake cells -- Almost all reduction cells use dry alumina scrubbers for control of emissions. Controls are required for the anode baking furnace as well as for the reduction cell. Hydrocarbon and SO_2 emissions are emitted primarily from this furnace and most are controlled by dry alumina scrubbers with the remainder using a wet conditioner followed by an ESP.

- Soderberg cells -- Hydrocarbons and SO_2 are emitted in the cell along with particulate matter and gaseous fluorides

    - Vertical studs: hooding fits close enough so that hydrocarbons are burned, leaving only carbon dust, SO_2 and gaeous fluorides. Controls include dry alumina scubbers, caustic scrubbers, and wet ESP's.

    - Horizontal studs: the cell exhaust is diluted with too much excess air so hydrocarbons do not completely burn. Subsequent condensation of tars on ducts and control equipment creates a serious tar fouling problem. Venturi scrubbers plus ESP or dry alumina scrubbers are used to avoid fouling the control device with tar.

These cell types are difficult to hood. Estimates have been made of the coverage, as listed in Table 3.

Because of the incomplete hooding, a large fraction of the emissions escape collection and are emitted through roof vents or monitors in the building. In some cases, roof scrubbers have been installed to remove the gaseous fluorides and particulate matter. It is also possible to collect these emissions in a duct along the roof line and remove the pollutants using high-efficiency scrubbers, bag filters, or wet precipitators. This type of fugitive emission control is costly but may be required to meet current standards (Ref. 5 and 7).

2.2 ALUMINUM INDUSTRY EMISSION FACTORS

The following subsection outlines the methodology involved in the development of size-specific emission factors for various processes within the primary aluminum industry. The data from which the emission factors are developed is reviewed, analyzed, and rated according to the guidelines

TABLE 2. SUMMARY OF AIR POLLUTION CHARACTERISTICS AND CONTROL

Process	Particulates	Gaseous fluorides	Hydrocarbons	Sulfur oxides	Control devices
Bauxite grinding	Yes	Neg[a]	Neg	Neg	ESP Venturi scrubber Bag filter
Calcining	Yes	Neg	Neg	Neg	Cyclones followed by ESP or bag filter
Anode baking	Yes	No	Volatiles	Yes[b]	Spray tower ESP (wet and dry) Self-induced spray Dry alumina adsorption
Prebake reduction	Yes	Yes	Carbon dust	Trace	Multiple cyclone Fluid-bed dry scrubber Coated filter dry scrubber ESP Spray tower Floating bed scrubber Chamber scrubber Vertical flow packed bed Dry alumina adsorption
Horizontal stud Soderberg reduction	Yes	Yes	Tars	Yes[b]	Spray tower Floating bed dry scrubber Wet ESP Floating bed wet scrubber
Vertical stud Soderberg reduction	Yes	Yes	Carbon dust	Yes[b]	Spray tower Self-induced spray Venturi scrubber Wet ESP Multiple cyclones Dry alumina adsorption ESP with dry alumina absorption
Materials handling	Yes	Neg	No	No	Spray tower Floating bed dry scrubber Quench tower and spray screen ESP

[a] Neg -- Negligible.
[b] In the form of SO_2 or H_2S.

TABLE 3. PARTICULATE EMISSION CAPTURE BY CELL HOODS

Pot type	Percent of particulates captured by best available hooding
New prebake	95
Older prebake	79
Vertical stud Soderberg	50
Horizontal stud Soderberg	85 to 90

established in the document "Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections" (Ref. 8).

2.2.1 Data Review

Data on size-specific emissions from processes within the primary aluminum industry are sparse. The data search yielded no data that could be given an "A" rating according to the criteria outlined in Section 1. Data collected is summarized in the following sections.

Kaiser Mead (Ref. 9)

The first data set was obtained from a report produced to document testing at the Kaiser Aluminum & Chemical Corporation's Mead works, a prebake primary aluminum reduction facility located approximately 15 miles north of Spokane, Washington. The test was conducted to measure fugitive particulate, fluoride, and SO_2 emissions being emitted through a roof monitor for determination of compliance with the State of Washington's Department of Ecology (WDOE) regulations. Testing was carried out in March 1982.

The plant has eight potlines, seven of which were in operation at the time of the test, producing 500 tons (450 Mg) of aluminum per day. Each potline has two potrooms, with an average of 71 operating pots per room. All pots within a line are hooded and served by two manifold systems which discharge into a common manifold. Eight four-sectioned baghouses draw exhaust from the common manifold via forced draft blowers. Aluminum ore is injected into the exhaust streams downstream of the fans, forming a fluoride-absorbing bed of alumina in each baghouse. The ore and entrained particulate matter are then collected in the bags. Gases that escape from the hooding system during the addition of Al_2O_3, tapping molten aluminum, or breaking the crust, are carried upward by natural convection and emitted through the roof monitor.

Coke for the anodes is received by the mill and fed through a rotary kiln. A cyclone is used to control emissions. The coke is then mixed to form an anode paste in the green carbon plant. Emissions from the mixing and handling operations are vented through a baghouse.

The formed anodes are then baked in the anode bake plant, which is normally fired by natural gas. Emissions are controlled by a baghouse, which has the same configuration as those used on the potlines.

Three 24-hr WDOE Method 13 particulate plus gaseous fluoride samples were collected from each of three roof monitor sampling points since the roof monitor area of 446.86 m^2 was divided into three zones. Three 24-hr particulate size samples were also collected using University of Washington Mark III cascade impactors at one of the sampling points, concurrent with total particulate testing.

Since percent isokinetic sampling flowrate values for WDOE Method 13 were not all within 100 ±10 percent and percent isokinetic sampling flowrate values for impactor sampling were not reported, this data is ranked B-quality since it was all taken for an extended period of time (24 hours) in an opening subjected only to natural convection (average velocity of 1.4 mps (4.5 fps)). On runs 1 and 3 the stainless steel substrates of the University of Washington Mark III Impactor were coated with Apizon H grease to minimize particle bounce and re-entrainment. No grease was used on Run 2 because of the large size of the particulate and the type of impactor used. The size percentage presented for 10 and 15 μm particulate is not as accurate for the lower end of the scale. The particle size distribution is presented in Table 4 and Figure 5.

Alcoa Badin (Ref. 10)

An extensive test program was carried out at Alcoa's Badin North Carolina prebake aluminum reduction facility to determine the size distribution of fugitive particulate exhausted through the potroom roof ventilator. The testing was carried out to develop a better understanding of the nature of the fugitive particulate and fluoride particulate matter, and to evaluate the accuracy of particulate determination from the monitor sampling manifold, EPA Method 14, which was developed primarily for determining fluoride emissions.

The aluminum reduction process at the Badin plant is similar to the process outlined for prebake reduction facilities in Section 2.1.2, but detailed process and emission control information was unavailable.

Testing was performed at the Badin facility using an Andersen In-Stack Cascade Impactor and a Bausch and Lomb analyzer. The Andersen sampler is an aerodynamic particle sizer with nine jet plates that divide the sample into eight fractions of particle sizes by weight and requires a lengthy sampling period of several hours. It does not lend itself to the sampling of the various short duration tasks conducted in a potroom but is well suited for long duration sampling. Since short duration task data was considered important, the Bausch and Lomb analyzer was also used. That analyzer consisted of a Bausch and Lomb Model 1300 ERC aerosol diluter and Model 40-1

TABLE 4. SUMMARY OF ACCEPTABLE DATA

Plant/type	Emission source	Run	Cumulative mass percent less than stated size (in microns) 0.625	1.25	2.5	5	10	15	Data Rank	Reference
Kaiser Mead/ prebake	Fugitive (roof monitor)	1	12	17	22	27	36	42	B	9
		2	8	10	14	21	29	35	B	
		3	14	19	25	32	45	53	B	
		Average	11	15	20	27	37	43		
Reynolds Longview/ HSS	Fugitive (roof monitor)	1	8	13	17	23	31	39	B	10
ALCOA Vancouver/ prebake	Fugitive (roof monitor)	1	11	13	19	30	43	52	B	11
		2	13	16	22	34	48	57	B	
		Average	12	15	21	32	46	55		
ALCOA Badin/ prebake	Fugitive (roof monitor)	Average of 20 short runs	17	25	43	70	91	96	B	12
Kaiser Tacoma/ HSS	Reduction cell (uncontrolled)	Average of 140 short runs	26	32	40	50	58	63	B	13

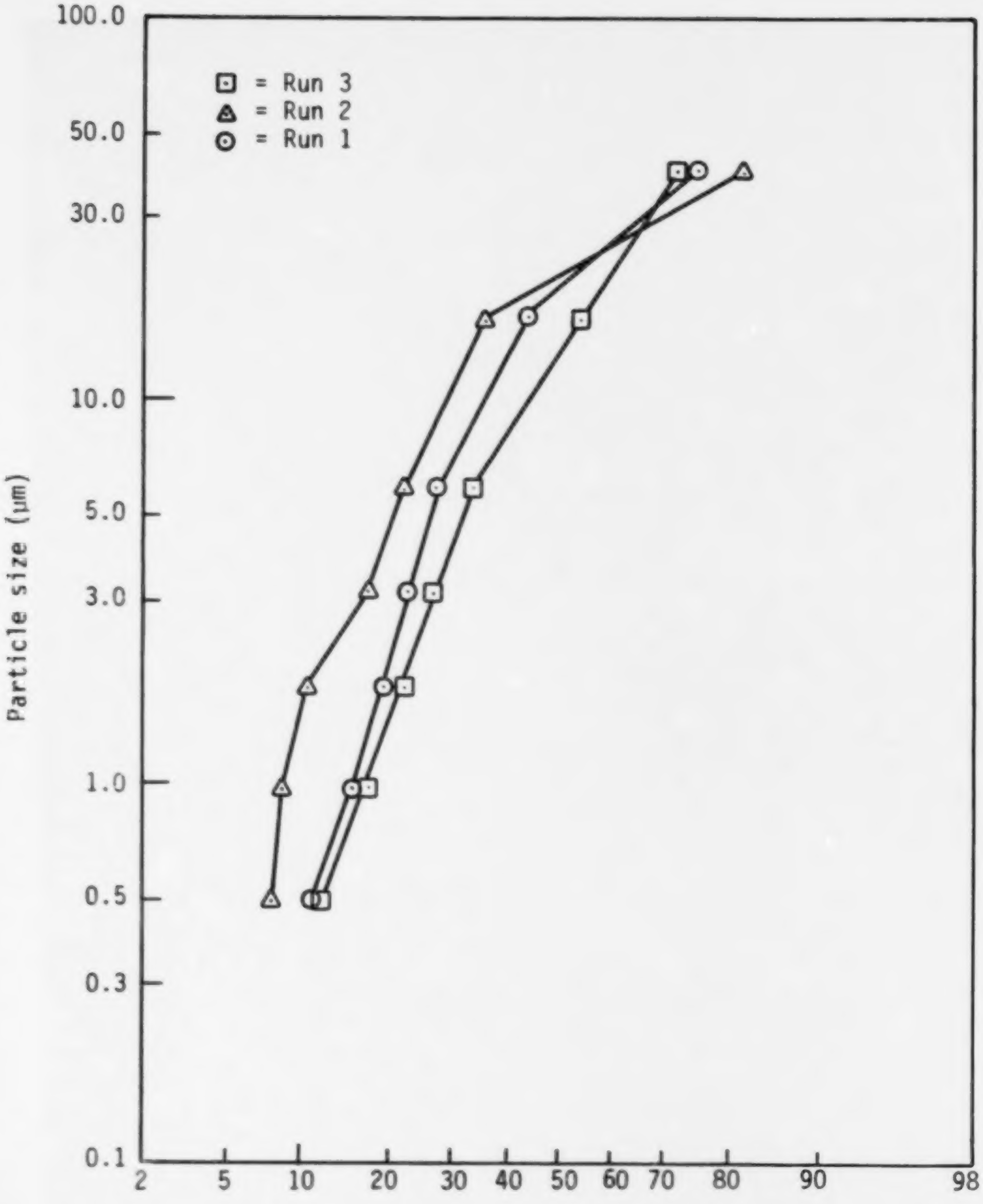

Figure 5. Particle size distribution for fugitive roof monitor emissions from the Kaiser Mead prebake aluminum plant.

29

particle counter, modified by the attachment of a multichannel electronic counter system, enabling the counting of particles in eight size fractions simultaneously.

The data gathered with the Bausch and Lomb was not considered for inclusion with the rest of the data since that equipment used an optical method for particle sizing. The data from the Andersen Impactor sampling was reduced and presented in limited tabular and graphical form. A search to obtain a more primary source of test data was fruitless. Due to the limited documentation available, these fugitive roof monitor emissions could only be considered as B-quality. Results are given in Table 4.

Alcoa Vancouver (Ref. 11)

Testing was performed at Alcoa's Vancouver aluminum plant by WDOE to determine particle sizes of fugitive emissions. The Vancouver facility is a prebake-type primary aluminum reduction facility located near the Columbia River, west of the city of Vancouver, Washington.

The plant has five potlines with 65 pots per room and two rooms per line. At the time of the test only two potlines were operating, producing approximately 133 tons (121 Mg) of aluminum per day. Emissions from the pots are collected by hoods and ducted to a reactor baghouse. There are five baghouses per potline and two stacks per baghouse. Prior to the baghouse, effluents from the pots are ducted to the reactors where they are passed through a fluid bed of Al_2O_3 for fluoride removal.

Most secondary emissions are released when the pots are drossed, tapped, or more Al_2O_3 is added. Emissions are carried to the ceiling by convection and released to the atmosphere through roof monitors. No control system is used with the roof monitors which are rectangular vents running the length of the roof of the potroom. On potroom no. 8, nine small diameter inlet ducts are connected and routed to a single 15-in. (38-cm) diameter stack located in the courtyard between potrooms no. 8 and 10 where samples were drawn for measurement of particulate and fluoride concentrations using EPA Method 14.

Three particle size samples were taken following WDOE Method 22. A University of Washington Mark III Impactor was used to collect all samples over a 50-hr period. Run 1 went from 12:10 to 21:30 on May 18, run 2 from 21:42 on May 18 to 12:06 on May 19, and run 3 from 12:12 on May 19 to 13:08 on May 20. For runs no. 1 and 2, the stainless steel substrates were coated with Apizon H grease to minimize particle bounce and reentrainment. No grease was used on run no. 3. Since it was noted that a large amount of loose material was in the first stage on run 3 and thought that some of the material may have migrated down from the other stages, Run 3 data was not included in the particle size determination. All three samples were taken at a point of near average velocity. Because of low stack temperature (about 90°F (32°C)) and the low moisture, the use of a heated probe and impingers for water collection was not required.

As with the other WDOE reports, percent isokinetic sampling rate values were not reported for this extremely low velocity stream. The overall procedure and equipment used, however, allow the particle sizing data for runs 1 and 2 to be ranked as B-quality. Results are given in Table 4.

Reynolds Longview (Ref. 12)

The second B-rated data set was obtained from a WDOE report produced to document compliance testing at the Reynolds Metals Company, Longview, Washington primary aluminum reduction plant. This facility incorporates HSS reduction cells. The purpose of the testing was to measure fugitive particulate emissions and gas velocity distribution across the roof monitor, and to compare two different methods for measuring fluorides. Testing was performed in February 1982.

The north plant has three potlines, with a combined capacity of 140,000 ton/yr (127,000 Mg/yr). The total output of the north and south plants is 210,00 ton/yr (191,000 Mg/yr). Each potline has four rows of 168 cells in two potrooms, or two 42-cell rows per potroom for a plant total of 504 cells. The potrooms have sidewall and basement ventilation. This facility was constructed in 1968.

The HSS cells are elevated slightly above the floor and have total-enclosure hooding with mechanically operated aluminum doors extending the full length of both sides of each cell. Pollutants continuously escape from the top of the cell enclosure and also from the hood doors when they are open. The doors have to be opened frequently to add Al_2O_3 to the Na_3AlF_6 bath by working the cell, to tap the molten layer from beneath the bath, and to insert and remove studs from the anode block while raising the flexible current connectors.

Four ducts, two on each end of each cell, pick up the primary exhaust from the top of the cell hooding enclosure and carry it to a manifold duct. One manifold handles primary exhaust from 14 cells, at a flowrate of 3,500 ft^3/min (100 m^3/min). Spray towers were used for primary pollution control until 1975. Wet ESP's are presently used to control primary emissions from the cells. Estimated control efficiency for the north plant primary control system is 90 percent. There is one sampling site on each ESP stack. There are three sampling sites evenly separated on each roof monitor.

All emissions not captured by the total enclosure hood are vented by convection through the secondary system, or roof monitors, which have no control. Each potroom has a roof monitor which is a hood opening 8 ft (2.4m) wide by 1,360 ft (415m) long running down the center of the roof. Three particulate/fluoride tests, which lasted approximately 1 day, were run at the potroom 52 center location, and on the final day a particle size test was run at the potroom 52 north location using the University of Washington Mark III Impactor. However, the particle size percent isokinetic sampling flowrate was not reported since the average velocity through the roof monitor was only 1.2 mps (4 fps) sampling was essentially for ambient particulate. As a result, the data can only be considered B quality, without a percent isokinetic sampling flowrate.

Each 1-day (24-hr) particulate/fluoride test set consisted of four samples, collected by four sampling trains separated by 2-ft (0.6m) intervals across the width of the roof monitor. Four samplers were used to determine differences in particulates. Two different types of particulate/fluoride sampling trains were used. The front half or nozzle and filter portions of the trains were identical in configuration, and consisted of a standard 0.500-in. (1.3-cm) ID nozzle followed by a filter-holder containing a preweighed 1.8-in. (47-mm) acetate filter. Particulate concentrations were determined by the particulate weight gains of the filter and a 50 percent aliquot of the nozzle rinse. The other 50 percent of the nozzle rinse, as well as the particulate filters, were sent to the DOE laboratory for fluoride analysis.

Table 4 summarizes the B-rated data collected during this testing.

Kaiser Tacoma (Ref. 13)

Testing at the Kaiser Aluminum and Chemical Corporation's Tacoma, Washington aluminum facility was initiated as a research project by the University of Washington to aid in the design of emission control equipment.

The Tacoma facility incorporates HSS reduction cells, however, process and production information at the time of the test were not provided.

Testing was performed with a University of Washington Mark II Cascade Impactor. A total of 140 particle size distribution tests of 4 to 6 minutes in duration were conducted and a composite size distribution curve was produced, taking into account the percentage of time each cell operation takes during a day.

An additional five data sets were reviewed for inclusion in this document but were rejected. In the Environmental Assessment Data System (EADS) Fine Paraticulate Emissions Inventory System (FPEIS) Series Report 139, three sets of fugitive emission particle size data were reported for the Reynolds Metal Company's Longview, Washington, plant which uses HSS aluminum reduction cells. A Nelson cascade impactor was used for particle sampling, but the sampling flowrate values were reported as being 194 to 197 percent (Ref. 14). These values were too large to allow use of the data.

EADS FPEIS Series Report 156 presented two sets of data for Kaiser's Mead, Washington Prebake plant. The primary uncontrolled emissions from the prebake reduction cells were collected with a Nelson cascade impactor with sampling isokinetic flowrate values of 297 to 299 percent (Ref. 15). These values are also too large to allow use of the data.

2.2.2 Data Analysis

Size-specific emission factors have been developed for each of the aluminum production emission sources where sufficient data were available to produce a size distribution curve in Section 2.2.1 (these data are summarized in Table 5). For the prebake plants, the data are presented graphically in Figure 9. Figure 6 represents the B-rated emission factor particle size curve for fugitive emissions and was obtained by taking the arithmetic average of the cutpoints of interest. For fugitive emissions from a HSS aluminum plant, the data are shown in Figure 7. The uncontrolled emissions factor particle size curve from a HSS aluminum plant is shown in Figure 8. The procedure used to develop the size-specific emission factors is discussed in this subsection.

Rating of Size-Specific Emission Factors

By combining the B-ranked test data for fugitive (roof monitor) emissions from prebake plants, coverage of prebake plants is sufficient to warrant a "C" rating for the developed cumulative size-specific emission factors by mass percent. The size-specific emission factors have been calculated by arithmetically averaging the B-rated size distribution data, developed in Section 2.2.1, at the cut points of interest (15, 10, 5, 2.5, 1.25, 0.625 µm). The cumulative mass percent less than the size of interest is then multiplied by the A-rated total emission factor presented in AP-42 and summarized in Table 6 to develop a C-rated size specific emission factor. Table 7 and Figure 9 present the C-rated size-specific emission factors.

Although B-ranked test data have been used to develop the cumulative size-specific emission factors by mass percent for fugitive (roof monitor) emissions from HSS aluminum reduction plants, the size-specific emission factors have been given a "D" rating, according to the criteria outlined in Section 1. The D rating was given because only one set of sizing test data was available although the total emission factor presented in AP-42 was A-rated. The specific emission factors may or may not be representative of the industry as a whole. Table 8 and Figure 10 present the D-rated size-specific emission factors for fugitive emissions from HSS aluminum reduction plants. The size-specific emission factors were calculated in the same manner as the prebake fugitive emission factors.

Finally, D-rated size-specific emission factors have been developed for the primary uncontrolled emissions from HSS aluminum reduction cells. The emission factors were given a D rating because the particle size distribution curve was obtained from an old report that had little particle sizing data process information for the tested facility, hence the representation of the industry as a whole by the emission factors could not be ensured.

The size-specific emission factors were once again calculated using the AP-42 total emission factors presented in Table 6. The analogous information for HSS aluminum reduction cells is presented in Table 9 and Figure 11.

TABLE 5. SUMMARY OF PARTICULATE EMISSION TEST DATA

Plant/type	Emission source	Control device[a]	Type of data[b]	Test date(s)	Test rating	Reference
Kaiser Mead/ prebake	Fugitive (roof monitor)	None	1,2	Mar 1982	A	9
Reynolds Longview/ HSS	Fugitive (roof monitor)	None	1,2	Apr 1982	A	10
ALCOA Vancouver/ prebake	Fugitive (roof monitor)	None	1	May 1982	B	11
ALCOA Badin/ prebake	Fugitive (roof monitor)	None	1	NA[c]	B	12
Kaiser Tacoma/HSS	Reduction cell	Uncontrolled	1	NA[d]	B	13

[a] None -- Control device not normally used.
Uncontrolled -- Testing performed at sampling point prior to control devices.

[b] 1 -- Particle size distribution.
2 -- Total particulate (lb/ton Al).

[c] Reference 11 fails to state test dates but based on publication date, testing was conducted prior to June, 1976.

[d] Reference 13 fails to state test dates but based on publication date and information in the publication, testing commenced no earlier than 1968 and was completed no later than November 1970.

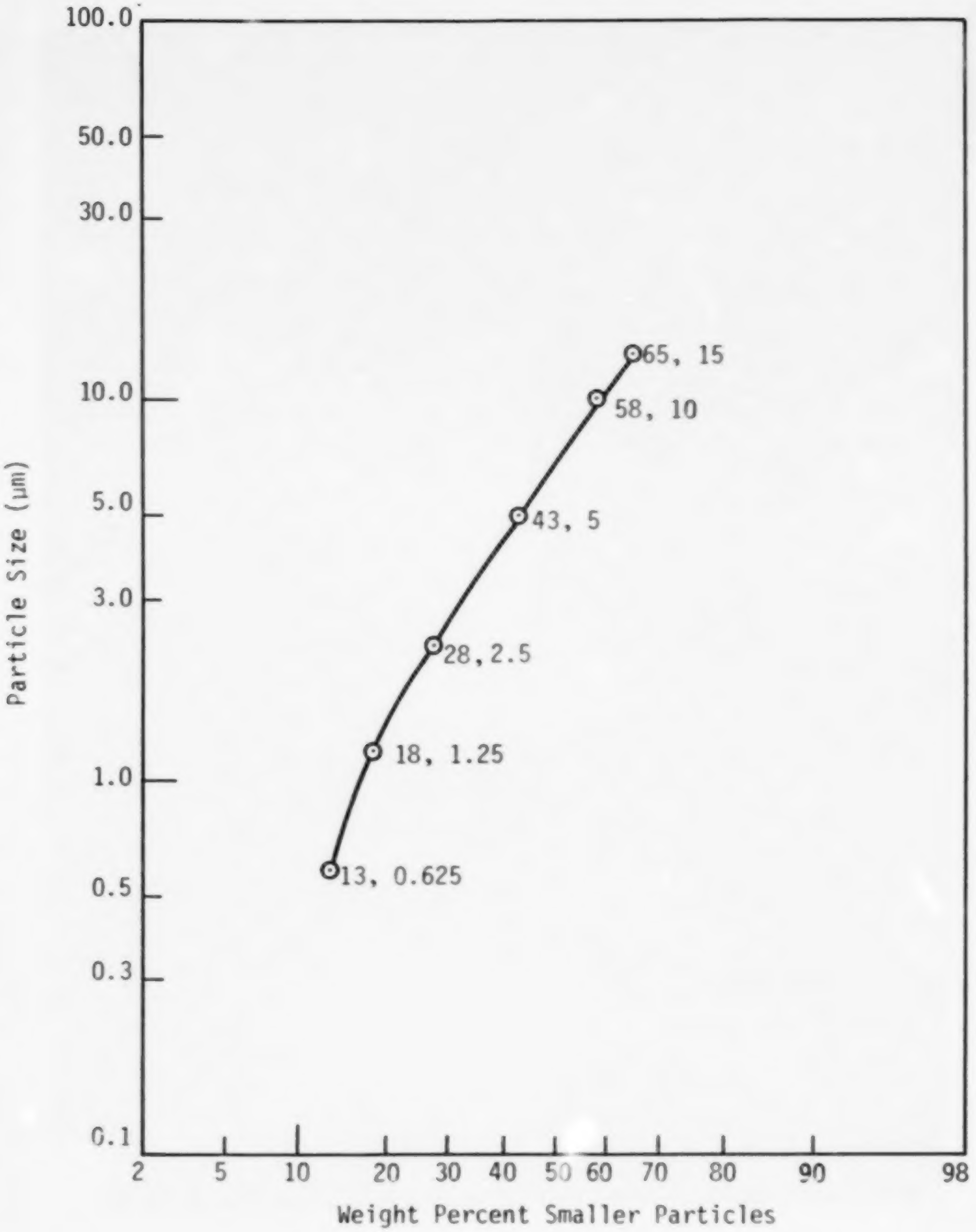

Figure 6. Average B-rated particle size distribution for fugitive roof monitor emissions from three prebake aluminum plants.

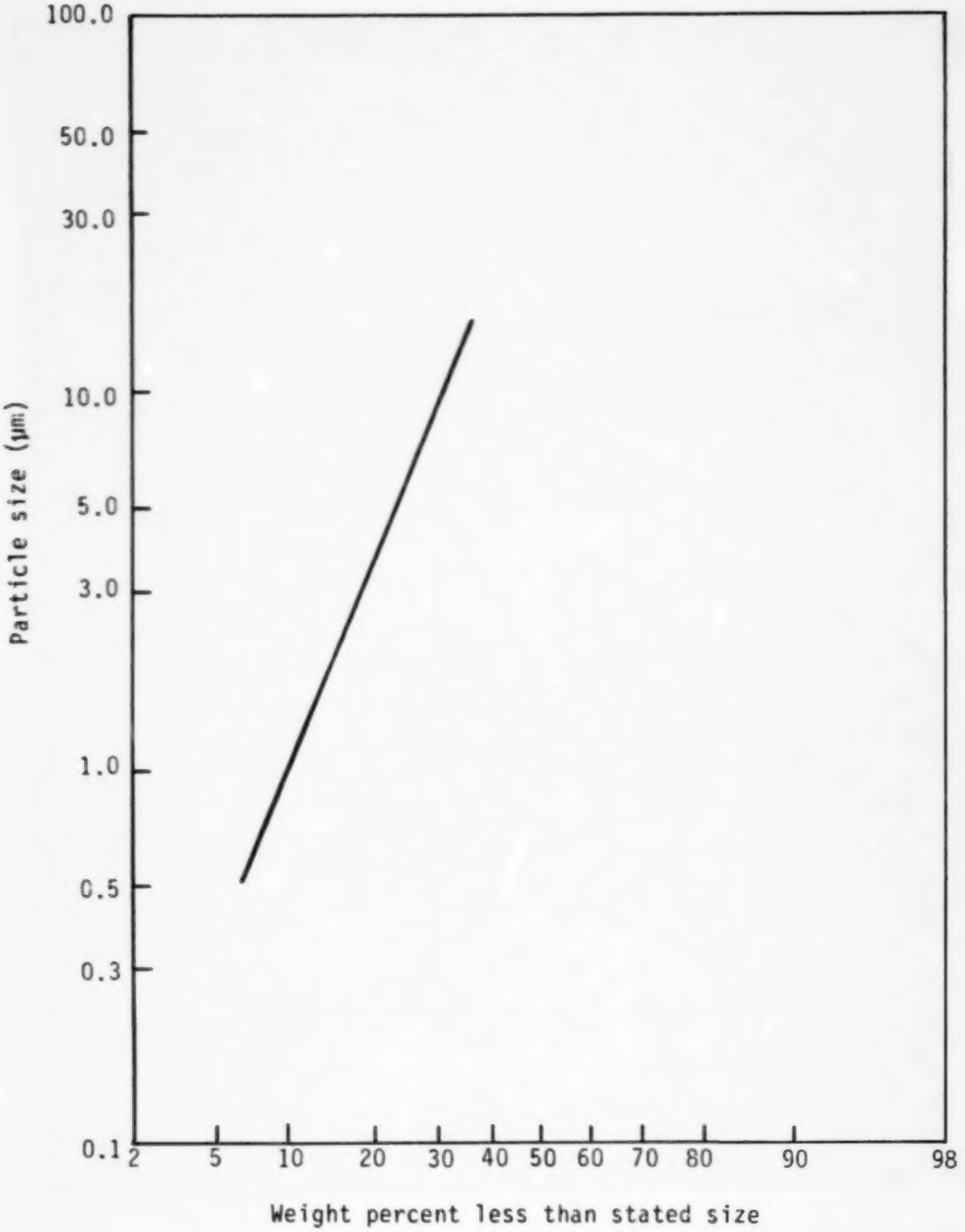

Figure 7. Particle size distribution for fugitive emissions from a HSS aluminum plant.

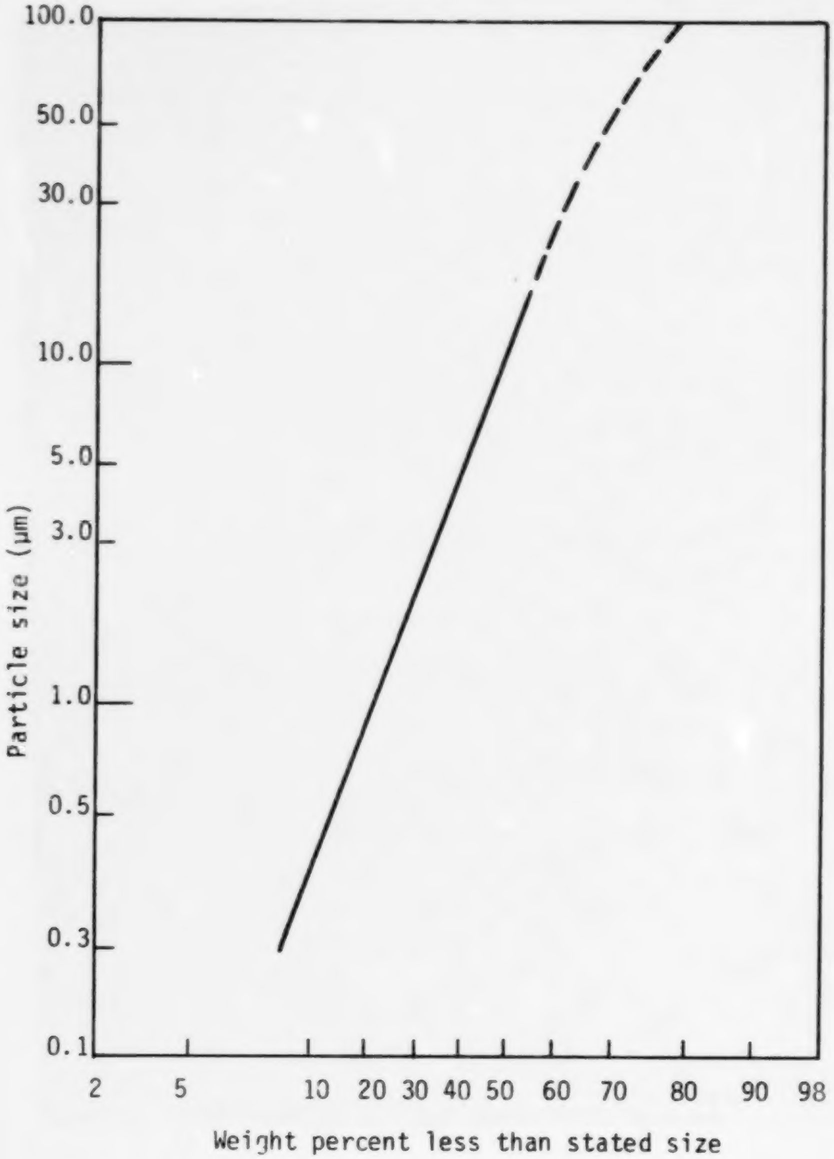

Figure 8. B-rated particle size distribution for primary uncontrolled emissions from an HSS reduction aluminum plant.

TABLE 6. EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION PROCESSES[a]

EMISSION FACTOR RATING: A

Operation	Total particulate[b]		Gaseous fluoride (HF)		Particulate flouride (F)		Sulfur oxides		Reference
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	
Bauxite grinding									
Uncontrolled	3.0	6.0	Neg	Neg	NA	NA	NA	NA	2,3
Spray tower	0.9	1.8	Neg	Neg	NA	NA	NA	NA	2,3
Floating bed scrubber	0.85	1.7	Neg	Neg	NA	NA	NA	NA	2,3
Quench tower and spray scrubber	0.5	1.0	Neg	Neg	NA	NA	NA	NA	2,3
Aluminum hydroxide calcining									
Uncontrolled	100.0	200.0	Neg	Neg	NA	NA	NA	NA	2,3
Spray tower	30.0	60.0	Neg	Neg	NA	NA	NA	NA	2,3
Floating bed scrubber	28.0	56.0	Neg	Neg	NA	NA	NA	NA	2,3
Quench tower	17.0	34.0	Neg	Neg	NA	NA	NA	NA	2,3
ESP	2.0	4.0	Neg	Neg	NA	NA	NA	NA	2,3
Anode baking furnace									
Uncontrolled[d]	1.5	3.0	0.45	0.9	0.05	0.1	c	c	4,10,11
Fugitive	NA	NA	NA	NA	NA	NA	NA	NA	
Spray tower	0.375	0.75	0.02	0.04	0.015	0.03	NA	NA	10
ESP	0.375	0.75	0.02	0.04	0.015	0.03	NA	NA	2
Dry alumina scrubber	0.03	0.06	0.0045	0.009	0.001	0.002	NA	NA	2,9
Prebake cell									
Uncontrolled	47.0	94.0	12.0	24.0	10.0	20.0	c	c	2,3,10,11
Fugitive	2.5	5.0	0.6	1.2	0.5	1.0	NA	NA	4,11
Emissions to collector	44.5	89.0	11.4	22.8	2.1	19.0	NA	NA	4
Multiple cyclones	9.8	19.6	11.4	22.8	9.5	4.2	NA	NA	4
Dry alumina scrubber	0.9	1.8	0.1	0.2	0.2	0.4	NA	NA	4,11
Dry ESP + spray tower	2.25	4.5	0.7	1.4	1.7	3.4	NA	NA	4,11
Spray tower	8.9	17.8	0.7	1.4	1.9	3.8	NA	NA	4
Floating bed scrubber	8.9	17.8	0.25	0.5	1.9	3.8	NA	NA	4
Coated bag filter dry scrubber	0.9	1.8	1.7	3.4	0.2	0.4	NA	NA	4
Cross flow packed bed	13.15	26.3	3.25	6.7	2.8	5.6	NA	NA	11
Dry + secondary scrubber	0.35	0.7	0.2	0.4	0.15	0.3	NA	NA	11
VSS cell									
Uncontrolled	39.0	78.0	16.5	33.0	5.5	11.0	NA	NA	4,11
Fugitive	6.0	12.0	2.45	4.9	0.85	1.7	NA	NA	11
Emissions to collector	33.0	66.0	14.05	28.1	4.65	9.3	NA	NA	11
Spray tower	8.25	16.5	0.15	0.3	1.15	2.3	NA	NA	4
Venturi scrubber	1.3	2.6	0.15	0.3	0.2	0.4	NA	NA	4
Multiple cyclones	16.5	33.0	14.05	28.1	2.35	4.7	NA	NA	4
Dry alumina scrubber	0.65	1.3	0.15	0.3	0.1	0.2	NA	NA	4
Scrubber + ESP + spray screen + scrubber	3.85	7.7	0.75	1.5	0.65	1.3	NA	NA	
HSS cell									
Uncontrolled	49.0	98.0	11.0	22.0	6.0	12.0	NA	NA	4,11
Fugitive	5.0	10.0	1.1	2.2	0.6	1.2	NA	NA	4,11
Emissions to collector	44.0	88.0	9.9	19.8	5.4	10.8	NA	NA	4,11
Spray tower	11.0	22.0	3.75	7.5	1.35	2.7	NA	NA	4,11
Floating bed scrubber	9.7	19.4	0.2	0.4	1.2	2.4	NA	NA	4
Scrubber + wet ESP	0.9	1.8	0.1	0.2	0.1	0.2	NA	NA	4,11
Wet ESP	0.9	1.8	0.5	1.0	0.1	0.2	NA	NA	11
Dry alumina scrubber	0.9	1.8	0.2	0.4	0.1	0.2	NA	NA	11

[a] For bauxite grinding, expressed as kg/Mg (lb/ton) of bauxite processed. For calcining of aluminum hydroxide, expressed as kg/Mg (lb/ton) of alumina produced. All other factors per Mg (ton) of molten aluminum product. Emission factors for sulfur oxides have C ratings. NA = not available.

[b] Includes particulate fluorides.

[c] Anode baking furnace, uncontrolled SO_2 emission (excluding furnace fuel combustion emissions):

20(C)(S)(1-0.01 K) kg/Mg [40(C)(S)(1-0.01 K) lb/ton]

Prebake (reduction) cell, uncontrolled SO_2 emissions

0.2(C)(S)(K) kg/Mg [0.4(C)(S)(K) lb/ton]

Where: C = Anode consumption* during electrolysis, lb anode consumed/lb Al produced
S = Percent sulfur in anode before baking
K = Percent of total SO_2 emitted by prebake (reduction) cells

[d] Uncontrolled rolled emission factor for aluminum hydroxide calcining represents emissions after a multicyclone

*Anode consumption weight is weight of anode paste (coke + pitch) before baking.

TABLE 7. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR FUGITIVE (ROOF MONITOR) EMISSIONS FROM PREBAKE ALUMINUM CELLS[a]

EMISSION FACTOR RATING: C

	Cumulative mass % <stated size	Cumulative emission factors	
		kg/Mg Al	lb/ton Al
Particle size[b] (μm)	Uncontrolled	Uncontrolled	Uncontrolled
15	65	1.62	3.23
10	58	1.45	2.90
5	43	1.08	2.15
2.5	28	0.70	1.40
1.25	18	0.46	0.92
0.625	13	0.33	0.67
Total	100	2.5	5.0

[a] References 9, 10, and 11

[b] Expressed as equivalent aerodynamic particle diameter

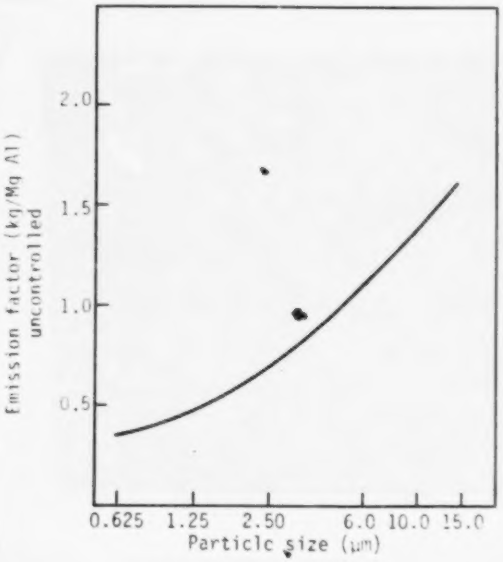

Figure 9. Cumulative emission factors less than stated particle size for fugitive emissions from prebake aluminum cells.

TABLE 8. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR FUGITIVE (ROOF MONITOR) EMISSIONS FROM HSS ALUMINUM CELLS[a]

EMISSION FACTOR RATING: D

Particle size[b] (μm)	Cumulative mass % <stated size	Cumulative emission factors	
		kg/Mg Al	lb/ton Al
	Uncontrolled	Uncontrolled	Uncontrolled
15	39	1.95	3.9
10	31	1.55	3.1
5	23	1.15	2.3
2.5	17	0.85	1.7
1.25	13	0.65	1.3
0.625	8	0.40	0.8
Total	100	5.0	10.0

[a] Reference 12

[b] Expressed as equivalent aerodynamic particle diameter

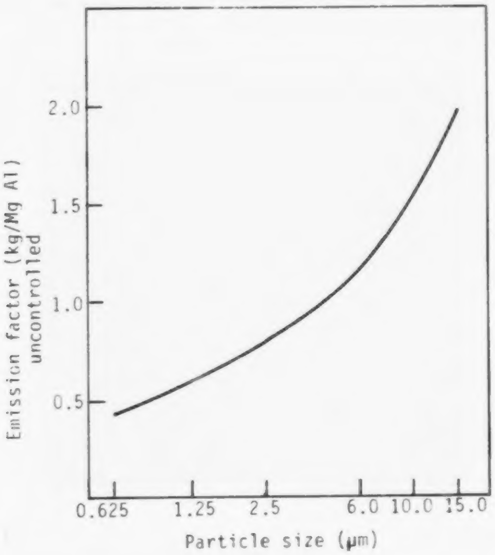

Figure 10. Cumulative emission factors less than stated particle size for fugitive emissions from HSS aluminum cells.

TABLE 9. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR PRIMARY EMISSIONS FROM HSS REDUCTION CELLS[a]

EMISSION FACTOR RATING: D

Particle size[b] (μm)	Cumulative mass % <stated size	Cumulative emission factors	
		kg/Mg Al	lb/ton Al
	Uncontrolled	Uncontrolled	Uncontrolled
15	63	30.9	61.7
10	58	28.4	56.8
5	50	24.5	49.0
2.5	40	19.6	39.2
1.25	32	15.7	31.4
0.625	26	12.7	25.5
Total	100	49.0	98.0

[a] Reference 13

[b] Expressed as equivalent aerodynamic particle diameter

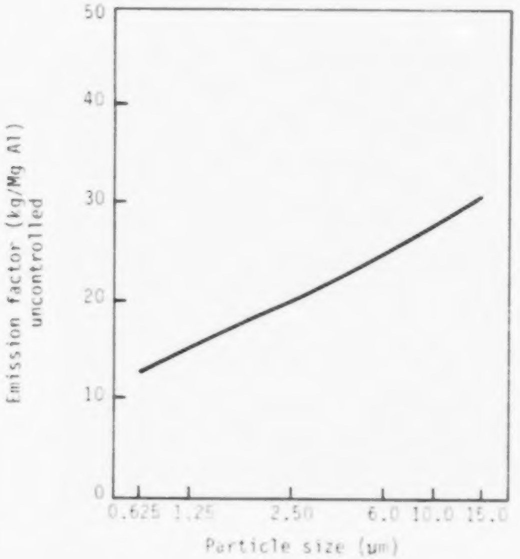

Figure 11. Cumulative emission factors less than stated particle size for primary emissions from HSS reduction cells.

A review of the size-specific emission factor development reveals a few interesting points:

- First, there are only a few published reports concerning particulate emissions from the aluminum industry, with even fewer test results available

- Second, those tests that have been performed are generally localized in the State of Washington

- Finally, no particle size or total particulate information was available for controlled emissions, except for the total particulate presented in AP-42, and repeated here in Table 6. It should be remembered, however, that roof monitor vents are typically several feet wide and at least a quarter mile long.

2.3 CHEMICAL CHARACTERIZATION

The largest particulate component is alumina. Fluoride components that have been identified include Na_3AlF_6, AlF_3, CaF_2, and chriolite ($Na_5Al_3F_{14}$). Other nonfluoride particulates are carbon, hydrocarbon tars, and iron oxides.

SECTION 3

PRIMARY COPPER INDUSTRY

The following section is a source category report for particulate matter emissions from the primary copper industry. The section includes a description of the primary copper industry and the various processes involved in primary copper production. Sources of particulate matter emissions from copper production processes are discussed, as well as the type of particulate matter emission control equipment used by the industry, for each process. Information concerning particulate matter emission rates and associated particle size distributions for the copper production processes studied is summarized and reviewed. Size-specific emission factors are then developed and rated according to the criteria outlined in Section 1. Finally, a revised AP-42 section on the copper industry is presented.

3.1 OVERVIEW

Production of primary copper normally begins with a concentration step, since the raw sulfide ores, from which the majority of copper is produced, generally contain less than 1 percent copper. The concentration step is typically performed at the mine site. The resulting concentrate is transported to the smelter. Most copper smelting is currently being accomplished with "conventional" pyrometallurgical methods that center on the energy-inefficient reverberatory furnace. Matte from the reverberatory furnace is converted to blister copper, and the blister copper is reduced, cast into anodes, and refined in electrolytic cells.

At six smelters, copper has been or is routinely produced by technologies newly introduced into U.S. production practice. One new smelter uses the Outokumpu flash smelting process. Another uses the Noranda continuous smelting process. Another installation has produced copper with a roast-leach-electrowinning technique. Three advanced hydrometallurgical processes are approaching semicommercial use. At present, these hydrometallurgical installations do not account for a sizable percentage of copper being produced (Ref. 16).

In 1983, 21 mines out of an estimated 35 principal mines accounted for 98 percent of the U.S. copper output. Virtually all copper ore was treated at concentrators near the mines. In 1981, concentrates were then processed by eight companies which operated 15 primary smelters. Listed in Table 10 are the primary copper smelter and copper refineries operating in the United States. Copper smelting capacity in 1981 totalled approximately 8.2 million

TABLE 10. U.S. PRIMARY COPPER PRODUCERS[a]

Company	Location	Description	Capacity, copper content (Mg/yr)
AMAX, Inc.	Carteret, New Jersey	Refinery	270,000
ASARCO, Inc.	Tacoma, Washington	Smelter	90,000
	El Paso, Texas	Smelter	105,000
	Hayden, Arizona	Smelter	165,000
	Amarillo, Texas	Refinery	380,000
Cerro Corporation	East St. Louis, Illinois	Refinery	100,000
Cities Service Company	Copperhill, Tennessee	Smelter	15,000
Copper Range Company	White Pine, Michigan	Smelter/refinery	80,000/80,000
Inspiration Consolidated Copper Company	Miami, Arizona	Smelter/refinery	135,000/65,000
Kennecott Copper Corporation	Garfield, Utah	Smelter	260,000
	Hayden, Arizona	Smelter	75,000
	Hurley, New Mexico	Smelter/refinery	75,000/95,000
	McGill, Nevada	Smelter	45,000
	Baltimore, Maryland	Refinery	250,000
	Magna, Utah	Refinery	170,000
Magma Copper Company	San Manuel, Arizona	Smelter/refinery	180,000/180,000
Phelps Dodge Corporation	Morenci, Arizona	Smelter	160,000
	Douglas, Arizona	Smelter	115,000
	Hidalgo, New Mexico	Smelter	125,000
	Ajo, Arizona	Smelter	65,000
	El Paso, Texas	Refinery	405,000
	Laurel Hill, New York	Refinery	85,000
Southwire Company	Carrollton, Georgia	Refinery	90,000

[a] Source: Reference 17.

Note: Refineries typically produce copper from both blister and scrap in varying proportions, and for this reason the U.S. Bureau of Mines does not categorize refineries as either "primary" or "secondary." In general, refineries located in Western states or adjacent to primary smelters process chiefly a blister feed, while those refineries in the East produce a higher proportion of copper from scrap.

tons (7.4 Tg) of raw ore, estimated to represent 1.9 million tons (1.7 Tg) of smelter product (blister copper). Refinery capacity totaled 2.6 million tons (2.4 Tg) of which approximately 88 percent was electrolytic refining and electrowinning capacity, and 12 percent was fire refining capacity (Ref. 17).

Several of the leading copper producing companies, shown in Table 10, are integrated, having mining, smelting, refining and fabricating facilities, along with marketing organizations. Others mine and process through the smelting or refining stage only (Ref. 18).

Advances in technology are likely to exert a large effect on all phases of the copper industry. Some of the changes, which are discussed later, appear inevitable from present trends, while others are only suggested from research. Compared to conventional smelting, the newer smelting processes are quite energy efficient and result in a 30 to 50 percent savings in energy costs. Both conventional and newer processes are quite flexible in their use of any form of fossil fuel. The adoption of the new smelting processes not only reduces emissions to the atmosphere but also reduces fuel requirements and the pollution that is generated from the fuel.

The emission of sulfur compounds, trace elements, and particulate matter to the atmosphere during smelting is probably the most pressing problem facing the copper industry. Insufficient control of such emissions has resulted in curtailment of production when necessary at some smelters owing to enforcement of national ambient air quality standards for SO_2. Construction of some new facilities had been delayed pending resolution of uncertainties surrounding new pollution standards and developments of the proper technology to meet the anticipated requirements (Ref. 18). The standard of performance for primary copper smelters promulgated in 1976 was reviewed in 1984. Based on the review, no revisions to the existing standards were considered necessary. However, substantial new construction is not expected since the demand for copper over the next 5 years can be met by existing domestic copper smelting capacity without the need for smelter expansion (Ref. 19).

The major disadvantage of the new pyrometallurgical processes is an unproven ability to handle impure concentrates (concentrates containing appreciable amounts of arsenic (As), antimony (Sb), bismuth (Bi), zinc (Zn), lead (Pb), selenium (Se), tellurium (Te), etc.). In many cases, when impurity concentrations are moderate (say, under 5 percent total impurities), impurities elimination is possible by making a matte in the new smelting unit and using a batch converting operation to volatilize these impurities (Ref. 20). In all cases, it is necessary to roast the concentrates and smelt the calcines in these new smelting units.

In general, the new smelting processes are capable of incorporating less recycled scrap than with conventional processing. However, several techniques; e.g., oxygen enrichment, are available. The use of these techniques can enable the new processes to recycle comparable quantities of scrap (Ref. 20).

Demand for copper for the year 2000 is forecast to be between 2.6 and 3.9 million tons (2.4 to 3.5 Tg), with the most probable demand within the range established at 3.1 million tons (2.8 Tg), representing a 1.1 percent annual rate of growth between 1981 and 2000. The growth rate in copper consumption in the United States had been 3 to 4 percent a year (Ref. 17).

3.1.1 Copper Production Process

The copper production process is discussed in this subsection and illustrated by a flow diagram in Figure 12.

Concentration (Ref. 16 and 20)

Sulfide ore from the mine is separated by the concentration process into two or more fractions. The fractions rich in valuable minerals are called concentrates, and the waste rock, low in metal content, is called the gangue. With this process, ore that usually contains less than 1 percent copper is concentrated into a fraction containing from 20 to 30 percent copper. At least 85 percent of the ore copper content is recovered in the ore concentrate.

Concentrating consists of milling the ore, crushing and grinding it to a fine powder, and then separating the minerals by froth flotation. In milling, the ore is sent through crushers and then through fine grinders. Between stages, the ore is classified (screened), and the final milled product is a mixture of particles between 65 and 200 mesh (210 to 74 μm) in size. In the last stages of milling, water is added along with chemicals to condition the ore for froth flotation.

Flotation is a continuous process that uses compressed air and various flotation chemicals to separate the ore into fractions. By proper selection of additives, certain minerals are caused to float to the surface and are removed in a foam of air bubbles, while others sink and are carried out with the slurry. The ore passes through many flotation stages to accomplish this separation. The chemicals that are added are classified as "frothers", which create the foam; "collectors", which cause certain minerals to float; and "depressants", which cause certain minerals to sink.

In the flotation of copper ores, the frothers most often used are reportedly pine oils, cresylic acid, or long-chain alcohols (Ref. 21). Lime is usually added in the final stages of grinding, both to adjust the pH of the slurry to an optimum level and to act as a depressant in conjunction with cyanide for iron pyrite (Ref. 21). Various xanthates or dithiophosphates act as collectors for the valuable sulfide minerals, and the copper and other recoverable minerals come off with the froth (Ref. 22). The gangue does not float and is discarded as "tailings".

After initial separation, the valuable minerals are sent through stages that further separate them by selective or differential flotation. By use of proper collectors or depressants, the concentrates may be upgraded to remove more iron pyrite. In some cases, other fractions high in Pb, Zn, molybdenum

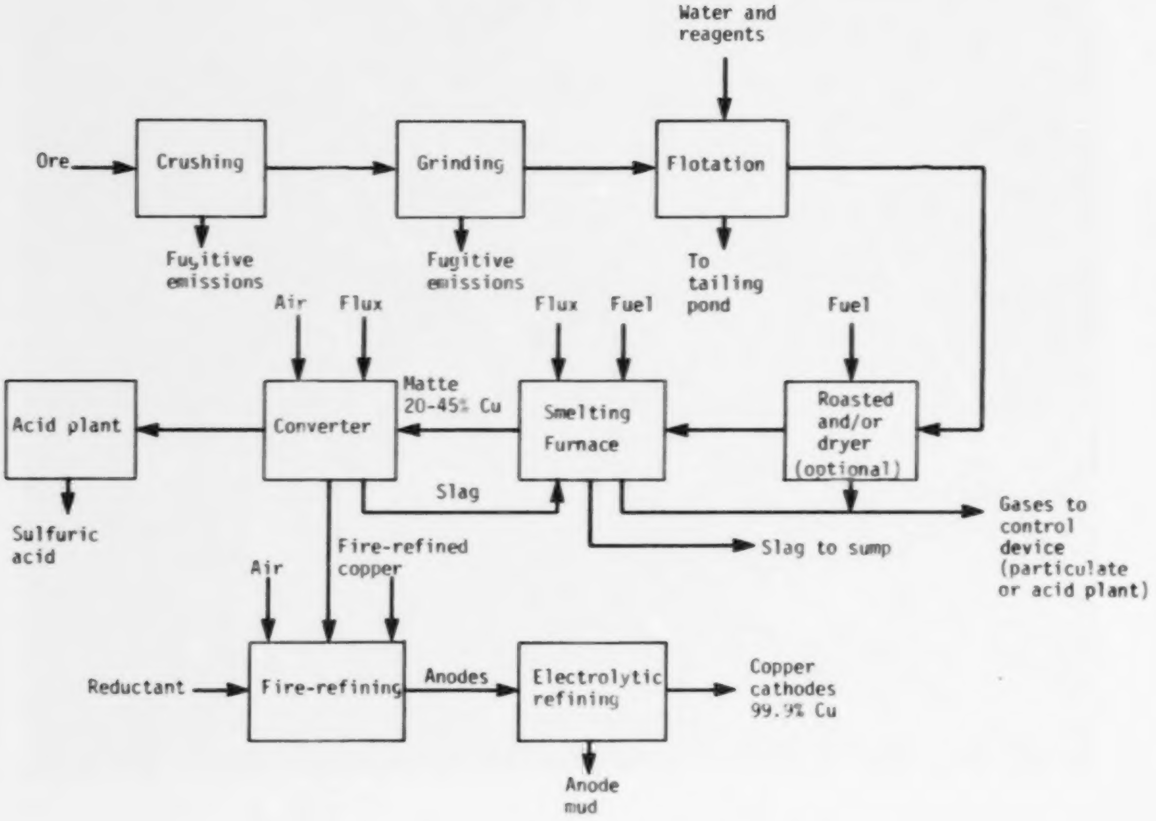
Water and reagents
Ore
Crushing
Grinding
Flotation
Fugitive emissions
Fugitive emissions
To tailing pond
Air
Flux
Flux
Fuel
Fuel
Acid plant
Converter
Matte 20-45% Cu
Smelting Furnace
Roasted and/or dryer (optional)
Sulfuric acid
Slag
Gases to control device (particulate or acid plant)
Slag to sump
Fire-refined copper
Air
Reductant
Fire-refining
Anodes
Electrolytic refining
Copper cathodes 99.9% Cu
Anode mud

Figure 12. Generalized copper production process flow diagram.

(Mo), or rhenium (Re), may be produced. These are usually sold to processors in the industries handling those metals. The copper ores of the west are a prime source for Mo; to separate this fraction, the concentrate must be steam stripped to remove the collector originally added (Ref. 23).

Occasionally, a concentrator will batch-treat a copper concentrate with cyanide to dissolve its silver and gold content. After separating the leached solution from the concentrate, zinc metal is added to reprecipitate the precious metals.

Concentrates are dewatered by clarification and filtration. They may be partially dried to simplify handling and shipment, or may be more completely dried for direct "green" feed to a smelting furnace. Ten of the 16 conventional smelters in this country have concentrator plants onsite or nearby.

Drying (Ref. 20)

The flotation concentrates received by the smelter are in the form of a wet filter cake and can contain 10 to 15 percent moisture. Cement copper (copper produced by acid leaching of oxide ores and precipitation with iron) can contain as much as 30 percent moisture. The charge to a reverberatory furnace can be dried so that its overall moisture content is 4 to 8 percent without unduly increasing dusting problems in the reverb. The removal of moisture in drying reduces the fuel requirements in the reverb. Also, the drier acts as a blender for homogenizing the charge. Rotary or multiple hearth driers are used for drying the feed materials (Ref. 20).

Roasting (Ref. 16 and 20)

About half the copper smelters in the United States roast their charge prior to feeding it to a reverberatory furnace. The older smelters use multiple hearth roasters for this purpose while two smelters use fluidized-bed roasters.

The objective of roasting copper sulfide ores and concentrates is to adjust the matte grade; i.e., the amount of sulfur and also remove certain volatile impurities such as Sb, As, and Bi. In the case of custom or toll smelters, the composition of feed materials can vary widely. Hence, roasting is practiced to blend and control the sulfur content of the charge. Depending on the impurity level, the grade of the concentrate can be controlled sufficiently at the concentrator to eliminate the need for roasting prior to reverberatory smelting.

In the multiple hearth roaster, concentrate is introduced at the top of a cylindrical vessel fitted with a series of round horizontal trays, or hearths. The ore is raked across each hearth in turn until it is discharged from the bottom of the cylinder. Air is admitted into the roaster, along with a fuel if necessary to maintain proper temperatures.

Most of the chemical reactions that occur in the roaster are with the iron sulfide or pyrite (FeS_2) in the concentrate rather than with the copper minerals. Copper has a higher affinity for sulfur, whereas iron combines preferentially with oxygen. Admitting a limited amount of air, therefore, causes the pyrite to oxidize, producing iron oxides (FeO and Fe_3O_4) and SO_2 (Ref. 22). The heat of the roasting process generally vaporizes much of the arsenic and some of the Sb and other elements in the ore. These "fumes" leave the roaster with the SO_2 gas. Multiple hearth roasting is currently in use at four domestic copper smelters. The roasters handle from 138 to 715 tons (125 to 650 Mg) of concentrate per day.

In the fluidized-bed roaster, the fluidizing gas is a recycled stream of flue gas, into which regulated streams of air and fuel gas are introduced. The solid is copper concentrate, continuously being fed and overflowing the fluidization vessel. Both the fuel and the oxygen are completely consumed; by elimination of excess air, the SO_2 content of the flue gas stream is greatly increased to a concentration great enough for feed to a sulfuric acid plant.

If the sulfur content of the concentrate is high enough, fuel is needed only at startup. With 20 percent sulfur in the feed, sufficient heat is released by the oxidation of sulfur to make additional fuel unnecessary. Operators of fluidized bed roasters, therefore, find it best not to process the ore into super-quality concentrates, but to tailor the quality of the concentrate to match the requirements of the roaster. Fluidized-bed roasters may not provide sufficient residence time for volatilization of certain substances such as arsenopyrites (Ref. 24).

Four domestic copper smelters have adopted fluidized-bed roasting. Units with capacities from 770 to 1,650 tons (700 to 1,500 Mg) per day are in use.

Both types of roasters (multiple hearth and fluidized-bed) usually operate at around 1,200°F (650°C). SO_2 concentration in the wet off-gas is usually 2 to 10 percent with multiple hearth roasters because of dilution with air. With fluidized-bed roasters, the wet off-gases can run 12 to 14 percent SO_2. Both types of roasters, therefore, can produce a steady stream of relatively rich off-gases suitable for sulfuric acid manufacture after cooling and dust removal. Both types of roasters involve handling and collecting of large quantities of hot abrasive dust, which can lead to high maintenance costs.

Reverberatory Smelting (Ref. 16 and 19)

Roasted and unroasted materials are melted after mixing with suitable fluxes in reverberatory furnaces. Liquid converter slag is also charged into the reverberatory furnace to recover its copper content. Heating of the charge is accomplished by burning fuel in the furnace cavity, the heat being transmitted to the charge primarily by radiation from the roof, walls, and flame. Reverberatory smelting is in use at 9 of the 15 smelters operating in this country.

Almost all the reverbs in the United States use natural gas as a fuel and only one plant uses powdered coal. Because of possible curtailment of natural gas, most smelters are now installing facilities to burn alternate fuels. The maximum smelting capacity of a reverb is limited by the amount of fuel that can be burned (a function of reverb shape and size) and the quantity of heat required by a unit weight of charge. Reverb throughput can be increased by drying and preheating the charge by roasting and preheating the combustion air.

In the reverberatory furnace, copper, iron, and sulfur form stable copper sulfide (Cu_2S) and stable ferrous sulfide (FeS), with excess sulfur leaving as SO_2. The combination of the two sulfides, known as matte, collects in the lower area of the furnace and is removed. Such mattes may contain from 35 to 65 percent copper, with 45 percent copper content being most common. Impurities such as S, Sb, As, Fe, and precious metals are also present.

The remainder of the molten mass (i.e., slag), containing most of the other impurities and being of lower specific gravity, floats on top of the matte and is drawn off and discarded. Slags in copper smelting are ideally represented by the composition $2FeO:SiO_2$, but contain alumina (Al_2O_3 from the various charge materials and calcium oxide (CaO) which is added for fluidity. Since reverb slags are discarded, the copper contained in the reverb slag is a major cause of copper loss in pyrometallurgical practice. The concentration of copper in the slag increases with increasing matte grade. This behavior limits the matte grades normally obtained in conventional reverberatory practice to below 50 percent copper.

When using a reverb for green charge smelting, 20 percent to almost 45 percent of the S in the feed is oxidized and is removed from the furnace with the off-gases. The wet off-gases can contain 1.5 to 3 percent SO_2. When using calcine smelting, SO_2 evolution is lower and about 10 to 15 percent of the S in the unroasted feed material is contained in the reverb off-gases. SO_2 concentration in the wet off-gases in this case can vary between 0.5 to 1 percent. In neither case is recovery as H_2SO_4 practical.

The hot gases from the reverb are cooled in waste heat boilers, which extract up to 50 percent of the sensible heat in the gases. A considerable amount of dust is removed in the waste heat boiler and the gases are further cleaned in ESP's before being vented to the atmosphere.

Reverberatory furnaces can vary in width from about 22 to 38 ft (7.1 to 12.3m) and in length from about 100 to 132 ft (32.3 to 42.6m). The roofs of the older reverberatory furnaces are sprung arch silica roofs, while almost all the newer furnaces have suspended roofs of basic refractory. Over the years, two types of reverberatory furnaces have evolved, each with its specific charging methods. The first and older is the deep bath reverberatory furnace which contains a large quantity (in excess of 100 tons (90 Mg) of molten slag and matte at all times. In modern deep bath reverberatory furnaces, the molten material is held in a refractory crucible with cooling water jackets along the sides to greatly diminish the danger of a breakout of the liquid material. In deep bath smelting, several methods exist for charging. Wet concentrates can be charged using slinger belts (high speed conveyors) that spread the concentrates on the surface of the molten bath. Dry concentrates or calcines from the roaster can be charged through the roof or via a Wagstaff gun, (an inclined tube). Roof charging (side charging) is rarely practiced in conjunction with deep bath smelting because of dusting problems with fine dry calcine and explosion problems with green charge. Wagstaff guns minimize these problems and are commonly used.

The second type of reverberatory furnace is the dry hearth type in which a pool of molten material exists only at the tapping end. Dry hearth furnaces are charged with wet or partially dried concentrates (green feed smelting) or with calcines through the roof. In the latter case the dusting problem can be quite severe for fine concentrates. The primary input material is the roasted or dried concentrate, not much different from the concentrate received from the mill. Slags from the converter and anode furnace are added for reprocessing, as are flue dusts from dust collection equipment throughout the smelter. Precipitates from hydrometallurgical operations or materials from refinery processing may be added at this step. At some smelters, impure scrap copper is reprocessed as part of the charge.

Flux normally consists of sand high in silica content, and usually limestone to make the slag more fluid. Sometimes "direct smelting ore" is used, which adds both fluxing material and additional copper.

When possible, the concentrate is charged into the furnace while still hot from the roaster (750°F (400°C) or more). Converter slag is charged as a liquid (2,000°F (1,100°C) approximately). Other materials are usually charged at ambient temperatures. The reverberatory furnace usually heats the mixed charge to at least 1,800°F (1,000°C) before the matte forms and separates; temperatures up to 2,400°F (1,300°C) have been reported. All operations are at or near atmospheric pressure.

Electric Smelting

Electric furnaces for copper smelting are similar to those used in other metallurgical industries. Capacities of up to 1,490 tons (1,350 Mg) of total charge per day are typical. The prinicpal input to the furnace is copper ore concentrates processed or blended to a suitable composition. Various fluxing materials are also required. The charge materials are similar to those outlined for a reverberatory furnace.

Electric smelting requires the use of carbon electrodes to conduct electric current into the layer of slag. Various types of carbon electrodes can be used. These electrodes are consumed during operation. The charge is usually heated to temperatures between 1,800° and 2,400°F (1,000° and 1,300°C), and the electric furnace is operated at a small negative pressure (Ref. 22). Electric furnaces are normally enclosed in a large building.

Flash Smelting (Ref. 16)

In flash smelting. ore concentrates are injected along with flux and preheated air into a combustion chamber. Part of the sulfur of the concentrate rapidly burns (hence, "flash" combustion) while the particles of charge are falling through the chamber. The heat from this combustion maintains the smelting temperature. Matte and slag form in the chamber and separate into layers as in a reverberatory furnace. The matte is sent to a conventional converter for further processing, and the slag, which contains too much copper to discard, is also further processed (as discussed later). One smelter in the United States is operating an Outokumpu flash smelting unit that was developed in Finland. This version is in extensive use in several other countries.

Another type of flash furnace is the Inco flash furnace which uses oxygen instead of preheated air for the combustion process. Two Inco flash furnaces are currently operating at U.S. smelters. The one at the Chino Mine Company has completed/replaced the two reverbatory furnaces at the site. Slag from the process has a low copper content and is discarded.

Copper concentrates especially tailored for flash smelting are the primary input. Not all concentrates are suitable for this process. The concentrates must be finely pulverized (50 percent minus 200 mesh (74 μm)), and must contain very low concentrations of Pb, Zn, and other volatile metals (Ref. 6). They must have a fairly high sulfur-to-copper ratio, and thus are not high-grade concentrates. The concentrates are not preroasted, unless they contain considerable As, but must be dried. Precipitates from hydrometallurgical operations cannot normally be handled by a flash smelter.

Flux in the form of silica sand or crushed rock must be prepared in a separate milling process to 80 percent through 14 mesh (1.30 mm) (Ref. 6) and must also be dried. High grade "direct smelting" concentrates can be substituted if available. Temperature in the flash chamber is maintained at approximately 2,000°F (1,100°C) (Ref. 22). Pressure is approximately atmospheric.

Converting (Ref. 16 and 20)

Matte produced in the reverberatory furnace is transferred in ladles to the converters using overhead cranes. The converters used in copper smelting are of the cylindrical Pierce-Smith type, the most common size being 13 ft by 30 ft (4.2m by 9.7m). Air is blown from the side through a series of openings called tuyeres. During the initial blowing period (the slag blow), FeS in the matte is preferentially oxidized to FeO and Fe_3O_4 and S is removed with the off-gases as SO_2. Flux is added to the converter to combine with iron oxide and form a fluid iron silicate slag. When all the iron is oxidized, the slag is skimmed from the furnace leaving behind "white metal" or molten Cu_2S. Fresh matte is charged into the converter at this stage and the slag blowing continued until a sufficient quantity of white metal has accumulated. When this happens the white metal is oxidized with air to blister copper during the "copper blow". The blister copper is removed from the converter and cast or subjected to additional fire refining prior to casting. Converter blowing rates can vary between 12,000 to 30,000 scfm (5.7 to 14.2 m^3/s) of air. Also, the SO_2 content of the off-gases is lower during "slag blow" than during "copper blow".

A variation on the Pierce-Smith converter is the Hoboken converter, used by one smelter in this country, though optimal operation of this converter has yet to be achieved. The principal difference between the two is that the flue that removes the gas from the converter is an integral part of the converter construction for the Hoboken type, instead of being a hood mounted above it. This design minimizes infiltration of uncontaminated air, losses of SO_2 from the converter mouth and allows production of a gas with a higher and more uniform SO_2 content.

To ensure that a slag of proper composition is formed and separated from the molten copper, converter temperatures are carefully controlled at 2,150° to 2,200°F (1,750° to 1,200°C) (Ref. 22 and 6). The converter operates at atmospheric pressure.

Noranda Process (Ref. 16)

The Noranda process is one design of a continuous smelter, which combines in a single furnace most of the functions of roasting, smelting, and converting (Ref. 25). This process approaches a one-step method of producing copper metal from ore concentrates. A Noranda installation is operating in Utah.

The Noranda furnace is a horizontal cylinder about 65 ft (21m) long, into which a mixture of concentrate and flux is continuously fed, along with fuel and oxygen. The furnace is fired from both end walls. The mixture reacts to form copper, matte, and slag, which separate into layers as in a batch smelting process. Additional oxygen-enriched air is blown through 63 side-mounted tuyeres into the matte layer, forming blister copper, which collects in a third liquid layer below the matte. Slag and copper matte are intermittently tapped from the furnace. Noranda slag contains 3 to 8 percent copper, and is processed to recover the copper content.

Noranda does not completely eliminate the use of the copper converter. Blister copper from Noranda contains from 1.5 to 2.0 percent S, and is usually batch treated in a standard converter to remove additional sulfur prior to fire refining. If the concentrate contains considerable impurity elements, the developer recommends that Noranda be used as a smelter only, to produce a high-grade matte for separate conversion to blister copper (Ref. 20). This is the mode of operation of the one U.S. facility (Ref. 26).

Slag Treatment (Ref. 16)

As mentioned previously, slag from a flash or Noranda continuous smelting process contains too much copper to justify disposal without some form of recovery. Also, in flash or continuous smelting there is no way to recycle the slag formed in the converter and the anode furnaces. Using an electric furnace is one of many ways to reclaim the copper content of these slags. This is the procedure being used with the flash smelter now operating in the United States.

In electric furnace slag treatment, coke is used to reduce sulfates and metallic copper and to reconstitute the copper as a sulfide. A molten matte is formed that can be recycled to a converter for production of copper metal; the process leaves a slag low in copper content that can be discarded.

The slags are similar to those from the reverberatory furnace, the copper converters, and fire refining furnaces, except with higher copper content. Flash smelting slags contain 1 to 2 percent copper, and slags from Noranda, 10 to 12 percent copper.

Carbon electrodes, as described for electric smelting, are consumed. Reported usage is 3.0 lb/ton (1.5 kg/Mg) of slag processed (Ref. 26). Iron pyrites are usually added to the furnace charge to adjust S content. The coke is similar to that used in electric furnace operations in other industries. High grade coal can be substituted.

The flotation slag treatment method is used at the Noranda process installation. As a molten slag cools, each constituent in the slag will solidify sequentially in an order determined by the freezing temperatures of the individual minerals. If the slag is cooled very slowly, crystals of relatively pure materials will form that are large enough to be separated by conventional concentrating procedures. Copper in the slag will form either as small particles of metallic copper or as crystals of copper-iron sulfide, both held in a matrix primarily of iron silicate.

Details of the existing U.S. process have not been released. It is believed, however, that molten slag from the Noranda furnace is to be transported while still molten to a series of deep covered pits, where over a period of days, or perhaps weeks, the slag will cool by natural conduction through the surrounding earth. When fully cooled, the slag will be reclaimed by conventional mining techniques, crushed, and concentrated. The resulting concentrate will be processed in smelting furnaces in the same manner as an ore concentrate (Ref. 20).

Acid Plants (Ref. 16)

Thirteen of the copper smelters in this country operate contact H_2SO_4 plants to treat all or part of the gases from the metallurgical operations. The heart of an H_2SO_4 plant is a fixed bed of vanadium pentoxide (V_2O_5) or other special catalyst which oxidizes the SO_2. All other components of the plant are auxiliary to this catalytic converter. The other components clean and dry the stream of gas, mix the proper amount of oxygen (O_2) with it (unless sufficient O_2 is present), preheat the gas to reaction temperature, and remove the heat produced by the oxidation reaction.

The plant incorporates one or two absorbers to contact the gas with water to form the acid. If only one absorber is provided, this is described as a single-contact H_2SO_4 plant. If two are provided, the second is placed between stages of the converter, and this is a double-contact plant. The second absorber allows a larger proportion of the SO_2 to be converted into acid, and thus removes more SO_2 from the gas stream if the initial concentration is high.

Three smelters in this country have constructed dimethylaniline (DMA) absorption plants, designed to handle waste streams that contain from 1.5 to 10 percent SO_2 although only one is in operation (Ref. 6). The DMA absorption process scrubs SO_2 from a stream of gas, then releases the SO_2 as a concentrated stream. The principal applications have been to concentrate streams for sulfuric acid manufacture, to absorb surges in waste gas flow that could not otherwise be handled by the acid plants, and to manufacture liquified SO_2 for sale.

Waste gases, after first being cleaned of particulate matter and dried, pass through a scrubber where most of the SO_2 is absorbed by DMA. The gases are then scrubbed with sodium carbonate (Na_2CO_3) to remove the remaining SO_2, then with weak H_2SO_4 to reclaim the DMA in the gas stream. The gases are then released to a stack. In a series of chemical operations, the DMA is recovered for recycling, and the SO_2 is recovered as dry, 100 percent SO_2 which is compressed, cooled, and stored as a liquid.

The DMA system has the advantage of being relatively insensitive to changes in SO_2 concentration of the gas stream, and to changes in gas flow rate. If part of a waste gas stream is sent directly to an acid plant at a constant rate, the DMA can handle the remaining gas, which may be of variable composition with uneven flow. The concentrated SO_2 from the DMA plant can be bled back into the acid plant stream as required to maintain a constant and higher SO_2 concentration. Thus the acid plant operates more efficiently and more of the SO_2 in the waste gas stream is recovered.

Refining (Ref. 20)

The blister copper produced by smelting is too impure for most applications and requires refining before use. It may contain silver (Ag) and gold (Au), and other elements such as As, Sb, Bi, Pb, Se, Te, and Fe. Two methods are used for refining copper -- fire refining and electrolysis.

The fire refining operation, which is the last major process that occurs at a copper smelter, employs oxidation, fluxing and reduction. It is based on the weak affinity of copper for oxygen as compared with that of the impurities. The molten metal is agitated with compressed air, SO_2 is liberated, and some of the impurities form metallic oxides, which combine with added silica to form slag. S, Zn, Sn, and Fe are almost entirely eliminated, and many other impurities are partially eliminated by oxidation. Pb, As, and Sb can be removed by fluxing and skimming as a dross. After the impurities have been skimmed off, copper oxide in the melt is reduced to metal by inserting green wood poles below the bath surface (poling).

Reducing gases formed by combustion of the pole convert the copper oxide in the bath to copper. In recent years, reducing gases such as natural gas or reformed natural gas have been used. If the original material does not contain sufficient Au or Ag to warrant its recovery, or if a special purpose silver-containing copper is desired, the fire-refined copper is cast directly into forms for industrial use. If it is of a nature to warrant recovery of the precious metals, fire refining is not carried to completion but only far enough to ensure homogeneous anodes for subsequent electrolytic refining.

In the electrolytic refining step, anodes and cathodes (thin copper starting sheets) are hung alternately in concrete electrolytic cells containing the electrolyte which is essentially a solution of copper sulfate ($CuSO_4$) and H_2SO_4. When current is applied, copper is dissolved from the anode and an equivalent amount of copper plates out of solution on the cathode. Such impurities as Au, Ag, platinum-group metals, and the selenides and tellurides fall to the bottom of the tank and form anode slime or mud. As, Sb, Bi, and nickel (Ni) enter the electrolyte. After the plating cycle is finished, the cathodes are removed from the tanks, melted, and cast into commercial refinery shapes. The copper produced has a minimum purity of 99.9 percent. The anode slime is treated for recovery of precious metals.

Twelve electrolytic refineries are operating in the United States (Ref. 17). Four are located near a copper smelter, and the others are distant from smelters.

Melting and Casting Cathode Copper (Ref. 16)

Refined copper from the electrolytic cells is melted and recast into the shapes required by fabrication industries. There is usually also a final adjustment of the oxygen content of the finished product.

Special equipment used for these operations range from direct-fired reverberatory furnaces to continuous casting machines. Electric arc and induction furnaces may be used to melt or hold the molten copper. The trend in this process is toward continuous or semicontinuous equipment to provide closer control of product quality and to minimize energy requirements.

Refinery Slimes Treatment (Ref. 16)

The first step in treatment of slimes from the cells of an electrolytic refinery is removal of the copper. This may be by direct roasting, or the slimes may be first leached with acid to extract a portion of the copper prior to the roasting step. The acid leach is accomplished in a pressure filter, through which sulfuric acid is circulated. Copper dissolves in the acid as a solution of $CuSO_4$. This solution is either mixed with the electrolyte in the refinery cells (Ref. 24) with the electrolyte purge to the liberator cells, or may be used for $CuSO_4$ production.

Roasting of slimes from the cells of an electrolytic refinery allows removal of the copper content. Heating the slimes in a strong acid environment converts the remaining copper to soluble $CuSO_4$, which can be removed by a subsequent water leach process (Ref. 27). Roasting also converts some of the Ag, and Te to soluble salts and volatilizes some of the Se.

The objective of the water leach process is to reprecipitate all the Ag and Te that has been made water-soluble in the roasting process, and to dissolve and separate all the soluble copper (Ref. 22).

Powdered copper is added to roasted solids in calculated quantity (Ref. 24). The mixture is then slurried with water in a tank, and by a cementation reaction, the Ag and Te are precipitated. The mixture is allowed to stand to cause these reactions to approach completion and to allow the solids to settle. The liquid is then decanted off, and the slurry is filtered. The liquid solution of $CuSO_4$ returns to the electrolytic cells or is used for $CuSO_4$ production. The filter cake is transferred to the Dore furnace.

Dore Furnace (Ref. 16)

This process separates the trace elements contained in the slimes into several distinct fractions, each of which is either sold or further treated. The most valuable fraction is a Dore metal, consisting primarily of Ag, Au, and the Pt group metals.

The equipment is a special small reverberatory furnace, which removes the groups of elements in separate slag-producing steps. The filter cake from the water leach process is mixed with a silica flux, charged into the furnace, and heated. A slag forms, primarily containing the Pb, Fe, As, and Sb (Ref. 22). This "sharp slag" is withdrawn and can be sent for further processing to a lead smelter. Sodium salts are then added to the furnace, and a soda slag forms. This slag contains Se and Te and any residual As and Sb (Ref. 27) and is further treated. An oxidative slag is then formed by blowing air through the molten metal (Ref. 24), removing Bi and any remaining copper. This slag is returned to the copper smelter. At least one refinery performs a final cleanup using Portland cement, which returns to the Dore furnace at the start of the next charge. The Dore metal that remains may be sold to a specialty processor, or may be further refined.

Roaster and Dore Furnace Gas Scrubbing (Ref. 16)

Gases from the slimes roaster and the Dore furnace contain particulates in quantities that justify their recovery for further processing. The gases also contain fumes, especially of Se, which hydrolyze in the water scrubber, allowing their separation for sale.

The scrubbers are generally of the water spray type (Ref. 24), with the water continuously recirculating. As solid material accumulates, periodic blowdown is performed. The amorphous Se is often removed by flotation

(Ref. 27). Occasionally the blowdown is combined with soda slag leach liquor. Wet electrostatic precipitators connectd in series with water scrubbers are also used for cleaning dore off-gas. Muds from the scrubber are recycled to the slimes roaster.

Other Processes Used in Primary Copper Production (Ref. 16)

Other processes used in the copper industry for copper production include sulfide ore leaching, vat leaching, cementation, solvent extraction, electrowinning, and Copper Leaching, Extraction and Refining (CLEAR). These are not discussed further because their use is limited and none emit significant amounts of particulate matter.

3.1.2 Particulate Emission Sources

This subsection describes the sources of controlled and fugitive particulate matter emission within the primary copper industry.

Concentration

The handling and milling of dry soil is the principal source of air pollutants in this process. Items of equipment are always enclosed, but transition between pieces of equipment are difficult to seal tightly. Ore classifiers are not always sealed. Both controlled and fugitive particulate matter emissions are liberated in this process.

Conventional Copper Smelting (Ref. 16, 20)

Figure 13 shows the sources of emissions in conventional copper smelting and refining. Emissions from each of the processes within conventional copper smelting and refining are discussed below by process.

Roasting and Drying

Particulate emissions from dryers typically consist of the fine particles present in the feed material. The particulate becomes very dusty when dried and is easily entrained by the off-gases. Calculations made for the dryer at Inspiration Consolidated Copper Company's Miami, Arizona smelter indicate as much as 20 percent of the feed becomes entrained in the off-gases (Ref. 28).

Roaster (Ref. 16)

Both controlled and fugitive particulate matter are emitted by multihearth roasters.

Particulate emissions from fluidized bed roasters are likely to be greater than from multihearth units, amounting to as much as 75 percent of the feed, because of the more complete separation of smaller particles from the body of charge. However fluidized bed roasters are equipped with cyclones for product recovery, reducing emissions to 15 percent of the feed.

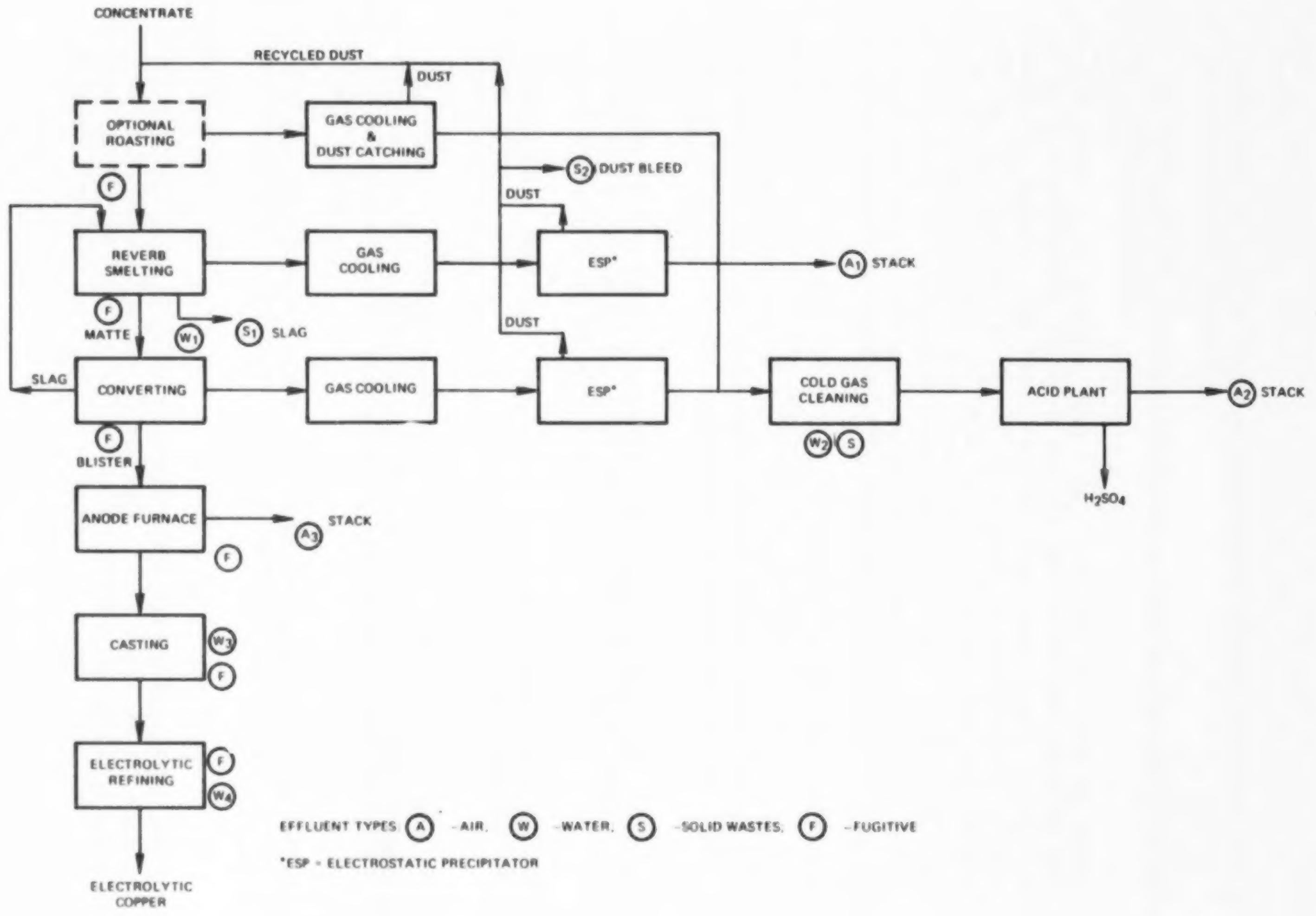
CONCENTRATE
RECYCLED DUST
DUST
OPTIONAL ROASTING
GAS COOLING & DUST CATCHING
S2 DUST BLEED
DUST
F
REVERB SMELTING
GAS COOLING
ESP*
A1 STACK
F
MATTE
W1
S1 SLAG
DUST
SLAG
CONVERTING
GAS COOLING
ESP*
COLD GAS CLEANING
ACID PLANT
A2 STACK
W2 S
F
BLISTER
H_2SO_4
ANODE FURNACE
A3 STACK
F
CASTING
W3
F
ELECTROLYTIC REFINING
F
W4
EFFLUENT TYPES A - AIR, W - WATER, S - SOLID WASTES, F - FUGITIVE
*ESP - ELECTROSTATIC PRECIPITATOR
ELECTROLYTIC COPPER

Figure 13. Sources of emissions in conventional copper smelting and refining.

Fugitive emissions may be evolved during the charging operation and transfer to the smelting furnace.

Smelting (Ref. 16)

Both controlled and fugitive particulate matter emissions are generated by the reverberatory furnace.

Two explanations have been proposed as causing the particle entrainment in the furnace offgases.

The coarser, or greater than 1 μm, fraction is caused by dusting of the flux and the mechanical stirring and disruption of the smelt by gas bubbles escaping the vessel. The fine fraction (less than 1 μm), is most likely formed by the condensation of the more volatile constituents of the dust in the gas stream (Ref. 28). If this is the case, the Southern Research Institute (SoRI) suggests that "the composition, size and concentration of the [offgases] all change with time" and that "under such conditions, long-term sampling or suitable averaging of the data is necessary to obtain data which accurately represent the emission".

Measurement of particle size distribution in the dust from the reverberatory furnace at the mouth of the furnace is apparently not possible due to the high temperatures (Ref. 28). However, all reverberatory furnaces are vented first through waste heat boilers before being vented to collection devices and a portion of the particulate is collected by the waste heat boilers (Ref. 16).

Because of the lower gas volumes and more uniform gas flow, particulate emissions are expected to be lower for electric furnaces, though no published estimates are available to verify this.

Particulate emissions from flash smelting furnaces have been reported to be about 6 to 7 percent of the feed, which is about the same for the reverberatory furnace (Ref. 16).

Particulate emission rates have not been reported, but are probably dependent on the size distribution in the feed. Since feed is continuously injected at high velocity into a moving gas stream, particulate loadings could be substantial.

Fugitive particulate matter emissions are evolved in the matte and slag tapping operations of all four types of smelting operations.

Converting (Ref. 16)

Relatively large amounts of particulate matter emissions are produced in both Pierce-Smith and Hoboken converters. This dust has also proven to be difficult to control because of its high resistivity and wide fluctuation in temperature (Ref. 29).

Fugitive particulate emissions are liberated from Pierce-Smith converters during molten copper matte and other material additions, since the converter mouth is rotated out from under the flue draft hood, and from both types of converters during slag and blister copper removal. In addition, particulate emissions result from leaks in the draft hood.

Baghouse or ESP's

Though all primary copper smelters vent offgases from drying, roasting, smelting, and converting either to baghouses or ESP's for particulate recovery and control while one smelter continues to use only a multicyclone. These devices are not 100 percent efficient and, therefore emit various quantities of particulate matter emissions.

Fire Refining and Anode Casting (Ref. 16)

Fugitive and controlled emissions are both produced by the fire refining and anode casting processes but detailed information regarding quantities and characterization is not available.

Melting and Casting Cathode Copper (Ref. 16)

Reverberatory furnaces, still occasionally used for refined copper melting, produce a gaseous discharge to the atmosphere, however the quality of this stream has not been reported. It may or may not contain significant (as high as 6 to 7 percent of the feed as per normal reverberatory furnace operation) quantities of particulate matter emissions.

Other Primary Copper Processes

Particulate matter emissions are also emitted from the Dore and gas scrubbing processes, however no detailed information is available for these sources.

3.1.3 Particulate Emissions Controls

Four types of emission control devices are used for particulate emissions cleanup within the primary copper smelting industry. These are discussed in the following paragraphs.

Baghouses

Baghouses are currently used at three smelters -- ASARCO-Tacoma and Inspiration. ASARCO-Tacoma's baghouse collects particulate from the multihearth roasters, Inspiration's baghouse from the dryer, ASARCO-El Paso's baghouse collects converter fugitive emissions, and Phelps Dodge Douglas' baghouse collects facility fugitive emissions. Before closing, the smelter at Anaconda, Montana, had a baghouse to collect particulate from the fluidized-bed roaster offgases and a portion of the electric furnace and converter offgases.

The application of baghouses at primary copper smelters generally calls for the use of a multicompartmented closed-pressure (rather than a closed-suction) design, because of the corrosion potential and the elevated dew point of the smelter offgases being treated . Baghouses used on dryers can be effective collectors, although potentially troublesome due to the formation on the bag of a caked product that must be redried (Ref. 16).

In general, baghouses are high efficiency collectors, achieving efficiencies of over 99 percent.

Cyclones

Cyclones are currently used in the primary copper industry on the following processes: ore milling, sizing and grinding, fluidized-bed roasters, dryers, an electric furnace, a Noranda reactor, and converters. They are typically used as precollectors, where the dust loadings from the processes are initially too high to be handled by the secondary collectors. The multicyclone unit on the converter at the Kennecott-McGill smelter is the only example of cyclones being the sole particulate control device. Cyclones are not currently used on multihearth roasters or reverberatory furnaces.

Fluidized-bed roasters, currently used at three copper smelters (Phelps Dodge-Morenci, Kennecott-Hayden, and Cities Services-Copperhill), are always fitted with cyclones, due to the large amount of particulate emissions, which can be as much as 75 percent of the feed (Ref. 16). At the Phelps Dodge-Morenci smelter, the cyclones on the fluidized-bed roaster are expected to have an efficiency of 92 percent removal at startup following annual shutdown for repair, which decreases to approximately 82 percent immediately before shutdown . The cyclones on the fluidized-bed roaster at Kennecott-Hayden have been reported to achieve a collection efficiency of 96.5 percent (Ref. 29).

Cyclones are used to control emissions from the dryers at Kennecott-Garfield, Kennecott-Hurley, and Inspiration. The collection of the particulates from dryers is complicated by the ready condensation of moisture in the warm effluent (Ref. 16). This creates potential problems of plugging for the cyclone. The five cyclones serving the dryer at the Inspiration smelter have a reported efficiency of 80 percent (Ref. 28).

Cyclones are used to control emissions from the Noranda reactor (furnace) at Kennecott-Garfield and the electric furnace at Inspiration. The design efficiency of the two cyclones at the Inspiration smelter is 80 percent (Ref. 28). At this smelter, one cyclone is in operation when the smelting rate is below 1,200 ton/day (1.1 Gg/day) of solids. If both cyclones are in operation at low gas flowrates, the pressure drop across the cyclones will be low and collection efficiency will be low (Ref. 30).

Cyclones are used at four smelters for the control of converter offgases -- ASARCO-Hayden, ASARCO-Tacoma, Kennecott-McGill, and Inspiration. The multicyclones serving the converter at McGill were rated originally at

85 percent efficiency, including dust settling in the flue prior to the unit. The operating efficiency has apparently not been determined.

Electrostatic Precipitators

ESP's are widely used throughout the primary copper smelting industry. Two conditions primarily affect the application of these devices -- the resistivity of the dust to be collected and the acid content of the offgases.

In general, the resistivity of the dust in smelter offgases is relatively high at reduced temperatures (195° to 392°F (90° to 200°C)) in the absence of natural conditioning agents such as moisture and SO_3. This relatively high resistivity is due to the presence of metal oxides. At higher temperatures, above 600°F (315°C), the resistivity of smelter dusts has been found not to cause collection problems (Ref. 30). Converter dusts, however, tend to cause problems, because of its high resistivity, especially during the slag blow (Ref. 31).

The use of SO_3 as a conditioning agent may cause problems when high levels of SO_3 are present. These problems include an increase in the corrosion rate resulting from a high sulfuric acid dew point and increasing the stickiness of the dust (SO_3 can sulphate the dust and thus make the dust difficult to handle). Many ESP's are operated at temperatures between 572° and 750°F (300° and 400°C) to avoid the sulfuric acid dew point, which can be around 312° to 428°F (156° to 220°C). If a smelter is forced to operate the ESP at lower temperatures to improve efficiency, acid mist can condense. Unless special steps are taken, such as using stainless steel construction, this will cause problems (Ref. 27 and 32).

Other factors that copper producers have attributed to good performance by ESP's include proper gas distribution and proper gas temperature as a result of continuous operation. Smelters have attributed poor ESP performance to factors such as intermittent operation, causing wide temperature fluctuations and leading to excessive corrosion and high adhesiveness of converter dust. This can cause buildups on the collecting electrodes, which will lead to short circuiting.

ESP's are used to clean up particulate emissions from dryers, converters, roasters and reverberatory furnaces, and flash furnaces.

Scrubbers

Application of scrubbers at primary copper smelters is used primarily for gas stream precleaning and to provide additional gas cooling prior to acid manufacturing . In addition, scrubbers are used as the final particulate control device prior to atmospheric emission on the dryer systems at the Kennecott-Garfield and White Pines-Michigan smelters and on one electric slag charging furnace at Phelps Dodge-Hidalgo.

3.2 COPPER INDUSTRY EMISSION FACTORS

All of the data readily available from the published literature concerning particle size distribution and mass emissions are summarized in this section and used to develop size-specific emission factors for primary copper industry processes. The emission factors are then ranked according to the criteria outlined in Section 1.

3.2.1 Data Review

Appropriate data from published literature are listed in this section by site and reference. The data are combined later to allow the generation of size-specific emission factors. The test on which these data are based involved the measurement of particulate mass, particle size and sulfur dioxide concentrations for slag and matte tapping operations at Kennecott Company's Hayden smelter (Ref. 33). Data from these tests are summarized in Table 11. The testing was performed to quantify the uncontrolled fugitive emissions from both operations and to develop emission factors for the tapping process as a function of the amount of slag or matte tapped. Measurements were made in December 1980 with a combined EPA Method 5 and 8 train for particulate and SO_2 emissions and with an Andersen 2000 Mark III in-stack cascade impactor fitted with a 15-μm cyclone precutter and straight sampling nozzle.

The copper production process at Hayden is as follows: copper ore is obtained from the Ray Mine located approximately 22 miles (35 km) from Hayden. The ore is crushed to minus 8 in. (20 cm) size at the mine and is transported by rail to the concentrator. There the ore is further crushed and milled prior to concentration. The concentrate is then dewatered and dried (6 to 12 percent moisture). The concentrates, together with precipitates from the mine's plant, are blended with silica flux and then fed to a Dorr-Oliver designed fluo-solids roaster (reactor) by a table feeder which controls the feedrate and maintains a seal on the roaster. The roaster feedrate typically ranges from 50 to 70 tons/hr (45.5 to 63.6 Mg/hr). Fluidizing air at about 15,000 scfm (7.1 m^3/s) is supplied through tuyeres at the bottom of the reactor vessel to keep the bed fluidized.

The fluidizing air reacts with the sulfur contained in the feed to form sulfur dioxide and calcine. Approximately 50 percent of the sulfur contained in the feed material is oxidized to sulfur dioxide. Because the reaction is exothermic, no auxiliary fuel is needed except during a cold startup. The bed temperature is generally maintained between 1,050 and 1,150°F (565 to 620°C). Most of the calcine produced exits the reactor as a fine dust suspended in the offgas stream. The offgases are ducted through a series of primary and secondary cyclones where approximately 95 percent of the suspended calcine is recovered and subsequently conveyed by screw conveyor to the calcine storage bin. The underflow from the roaster is reclaimed through an underflow screw and transported to the calcine storage bin by a drag chain conveyor.

TABLE 11. SUMMARY OF KENNECOTT COMPANY DATA (HAYDEN, ARIZONA)[a]

		Cumulative mass percent less than stated size (microns)						
Emission source	Sampling run	0.625	1.25	2.5	5	10	15	Data rank
Fugitive -- reverberatory furnace matte tapping	1	58	61	63	66	68	70	B
	2	77	79	80	82	84	86	B
	3	80	82	84	86	88	89	B
	4	46	47	51	53	56	58	A
	Average	65	67	69	72	74	76	
Fugitive -- reverberatory furnace slag tapping	1	19	22	24	26	29	33	A
	2	7	9	9	11	16	20	A
	3	28	32	35	39	43	46	A
	4	14	18	21	23	26	31	A
	Average	17	20	20	25	28	33	

[a] Source: Reference 33.

Calcine, precipitator dust, and flux are then fed to a single reverberatory furnace for smelting. The reverberatory furnace, a suspended arch design, is charged at approximately 1,100 to 1,200 ton/day (1.1 Gg/day) through two openings by a pair of Wagstaff feeders. The furnace is charged at approximately 15-min intervals for a duration of 2 to 3 min. The furnace is fired with natural gas, but it is equipped with oil burners in the event gas service is interrupted. Both matte and slag are tapped by way of tap holes in the side of the furnace. The molten material flows down its respective launder (chute) into a ladle which is positioned one floor below the tap hole. The slag ladle is transported by a hauler to the slag dump (average 650 ton/day) (590 Mg/day). The hauler has the capability of weighing each ladle of slag (±0.5 ton (450 kg)). The matte ladle has a capacity of 18 tons (16 Mg) of matte and each ladle is usually filled to capacity. Transport of the matte ladle to the converter aisle is accomplished using a short shuttle carriage and an overhead crane.

Although the data were graphically presented in Ref. 33, they were read at desired cutpoints for inclusion in Table 11. The cumulative size-specific particle size distribution data for fugitive emissions during reverberatory furnace matte tapping operations include three data sets ranked B-quality since the percent isokinetic sampling rate was less than 90 percent, and one data set ranked A-quality. All cumulative size-specific particle size distribution data for fugitive emissions during reverberatory furnace slag tapping operations had percent isokinetic sampling flow rate values ranging from 97.1 to 100.3 percent and were ranked A-quality.

ASARCO -- Tacoma, Washington (Reference 34)

Although particle size data for combined emissions from roasting, reverberatory smelting, and arsenic recovery are available from ASARCO's Tacoma, Washington plant, these data are not used further to develop emission factors because the arsenic plant emissions are not normally combined with the other flue gases.

Particle size distribution data for emissions from the combined roaster and reverberatory processes were obtained in September 1973, and are summarized in Table 12. The lack of reported isokinetic sampling rates reduces the quality of the uncontrolled (ESP inlet) and controlled (ESP outlet) emissions to B-quality.

Particle size distribution data for emissions from the converting operation were obtained in September 1973. Since the test conditions were not extensively reported but the sampling isokinetic flowrate values were both 104 percent, both the ESP controlled and uncontrolled samples are considered B-quality.

Phelps Dodge -- Playas (Ref. 35 and FPEIS Run No. 349)

An emissions testing program was conducted at the Playas, New Mexico copper smelter facility of Phelps Dodge on July 25 and 26, 1978. The process

TABLE 12. SUMMARY OF ASARCO CORPORATION DATA (TACOMA, WASHINGTON)

Emission source	Sampling run	Cumulative mass percent less than stated size (microns)						Percent isokinetic sampling flowrate value	Data rank	FPEIS number
		0.625	1.25	2.5	5	10	15			
Roaster and reverberatory furnace and arsenic plant										
ESP inlet[a]	1/23/75	4	13	29	45[b]	54	66	128	B	144
ESP inlet[a]	1/23/75	6	17	35	52[b]	60	71	127	B	144
ESP outlet[a]	1/20/75[c]	67	85	92	95[b]	96	97	52	B	144
ESP outlet[a]	1/21/75[c]	62	78	88	92[b]	93	95	41	B	144
ESP outlet[a]	1/21/75[d]	72	86	90	91	93	96	NR	B	--
Roaster and reverberatory furnace										
ESP inlet[e]	9/25-26/73	25	66	97	100	100	100	NR	B	--
ESP outlet[e]	9/26/73[f]	66	74	77	99	100	100	NR[g]	B	6
	9/25-26/73	58	78	91	97	99	100	NR	B	--
Converter										
ESP inlet[e]	9/25-26/73[h]	1	3	12	32	59	NR	104	B	7[i]
ESP outlet[e]	9/25-26/73[h]	30	42	56	72	99	100	104	B	7[i]

[a] Source: Reference 34.

[b] Reported at 6 μm by FPEIS and not adjusted to 5μm.

[c] Nelson cascade impactor.

[d] UW Mark II impactor.

[e] Reference 36.

[f] Andersen Mark III.

[g] NR -- not reported.

[h] Brink model BMS-11 impactor.

[i] FPEIS data reduction not used due to apparent data input errors.

tested was a secondary converter hooding system which removed fugitive emissions from the converter during the slag and copper below cycles. No process data was reported and sampling conditions were minimally reported. All percent isokinetic sampling flowrate values however were reported as being 99 percent as listed in Table 13. A Brink Model B impactor was used for particle sizing. Although sampling and process conditions should be better documented, this data is considered A-quality due to the use of an acceptable impactor with an acceptable sampling flowrate.

Kennecott -- Garfield (Ref. 37,38)

Flue dust at Kennecott Copper Corporation's Utah smelter was characterized prior to July 1976 using an Andersen cascade impactor. The smelter used a process for the reduction of copper concentrate termed "green feed smelting." Unroasted ("green") copper concentrate was fed directly into reverberatory furnaces. The copper-iron sulfide matte was periodically tapped and transferred to barrel-type Pierce-Smith converter furnaces for conversion to blister copper.

The particle sizing information from this report only summarizes the data and presents it in a graphical form. The usefulness of these data are reduced without knowing sampling dates, sampling duration, number of samples, percent isokinetic sampling flowrate values, and smelter operating conditions. By assuming a particle density of 4 grams per cubic centimeter, a correction is required in order to obtain equivalent aerodynamic particle size which assumes particles have a density of 1 gram per cubic centimeter. The additional information is likely to exist only in the files of Kennecott Copper. Based on these limitations the averages presented in Table 14 can only be ranked as D-quality data. (Since these data were collected, this smelter has been modernized and is now a Noranda reactor system).

ASARCO -- Hayden (Ref. 33)

Prior to December 1979, ASARCO conducted particle size distribution tests at its Hayden smelter as shown in Table 15 on an ESP serving both the roaster and reverberatory furnace and an ESP serving a copper converter. Although the sampling was conducted using a Mark III impact sampler with a pre-impactor and Reeve Angel substrates, the subtrates were not properly conditioned prior to sampling and no isokinetic sampling flowrate value was reported, hence the data is a low D-quality.

Phelps Dodge -- Ajo (Ref. 39)

Tests were conducted during July 9 and 10, 1976, on the ESP treating offgases from the reverberatory furnace at the Phelps Dodge-Ajo smelter. The tests revealed an overall, in-stack collection efficiency of 95.7 percent, with a range of efficiencies from 94.1 to 97.4 percent.

Additional tests were run on July 15, 1976, to determine the amount of particulate which condenses by cooling the flue gas from in-duct temperatures (e.g., 600°F) to out-of-duct temperatures (e.g., 250°F). With the

TABLE 13. SUMMARY OF PHELPS DODGE DATA[a] (PLAYAS, NEW MEXICO)

Emission source	Sampling run	Cumulative mass percent less than stated size (microns)						Percent isokinetic sampling flowrate value	Data rank
		0.625	1.25	2.5	5	10	15		
Converter									
Fugitive slag/ copper blow	1	44	54	55	79	100	100	99	A
	2	41	53	64	81	89	94	99	A
	3	29	34	61	100	100	100	99	A
	Average	38	47	60	87	96	98		

[a]Reference 35.

TABLE 14. SUMMARY OF KENNECOTT COPPER DATA[a] (GARFIELD, UTAH)

Emission source	Cumulative mass percent less than stated size (microns)						Data rank
	0.625	1.25	2.5	5	10	15	
Reverberatory furnace							
ESP inlet	60	71	75	79	83	NE[b]	D
ESP outlet	66	75	82	90	93	NE	D
Converter							
ESP inlet	43	65	75	81	88	NE	D
ESP outlet	30	52	62	72	80	NE	D

[a]References 37,38. All sampling conducted prior to July 1976.

NE = not estimated due to excessive extrapolation

TABLE 15. SUMMARY OF ASARCO CORPORATION DATA[a]
(HAYDEN, ARIZONA)

Emission source	Sampling run	Cumulative mass percent less than stated size (microns) 0.625	1.25	2.5	5	10	15	Data rank
Roaster and reverberatory								
ESP Inlet	1	8	15	22	31	41	49	D
ESP Outlet	1	29	37	47	53	65	70	D
Converter								
ESP Inlet	1	50	62	74	81	89	91	D

[a] Reference 33.

condensibles, the average collection efficiency is reduced to near 50 percent.

Particle size distributions at the inlet and the outlet of the ESP were determined during the July 9th and 10th tests and the average values were present. These results are summarized in Table 16. Since there is no sampling data including the sampling isokinetic flowrate values, this data can only be considered C-quality.

MAGMA -- San Manuel (Ref. 40)

Particle size tests were made on the outlet of the ESP serving the reverberatory furnace at the Magma smelter during the period April 14 to April 23, 1980. The average size data is presented in Table 17. The particulate collected had a mean diameter of approximately 2.75 microns with 64 percent of the particles less than 5.0 microns in diameter. Since no sampling data was presented, this data can only be considered C-quality.

3.2.2 Data Analysis

This subsection discusses the development of cumulative size specific emission factors for the primary copper production processes discussed in Section 3.2.1.

D-rated cumulative size specific emission factors have been developed for uncontrolled fugitive emissions from matte and slag tapping operations of the reverberatory furnace. (The ratings and calculation procedures are outlined in Section 1. Tables 20 and 21 present the particulate mass

TABLE 16. SUMMARY OF PHELPS DODGE-Ajo DATA[a]

Emission source	Sampling run	Cumulative mass percent less than stated size (microns) 0.625	1.25	2.5	5	10	15	Data rank
Reverberatory furnace								
ESP Inlet		9	16	21	23	27	NE[b]	C
ESP Outlet		43	59	70	75	79	NE	C

[a] Reference 39.
[b] NE = Not estimated due to excessive extrapolation.

TABLE 17. SUMMARY OF MAGMA (SAN MANUEL) DATA[a]

Emission source	Sampling run	Cumulative mass percent less than stated size (microns) 0.625	1.25	2.5	5	10	15	Data rank
Reverberatory furnace								
ESP Outlet		NE[b]	22	42	64	78	83	C

[a] Reference 40.
[b] NE = Not estimated due to excessive extrapolation.

emission factors as presented in the most recent version of AP-42 for primary copper production operations and fugitive emissions.) A- and B-quality cumulative particle size distribution data obtained at the Hayden, Arizona facility of the Kennecott Company was combined with B-rated particulate matter emission factor ratings. The resulting size specific emission factors are D-rated due to the use of limited high-quality size distribution data. The size-specific emission factors are presented in Tables 18 and 19 and shown graphically in Figures 14 and 15.

E-rated cumulative size specific emission factors have been developed for uncontrolled and ESP-controlled multihearth roaster and reverberatory smelter operations as shown in Table 22 and Figure 16. Only the B-quality cumulative particle size distribution data was used. The distribution data was combined with a B-rated particulate matter emission factor and an estimated emission factor to develop uncontrolled and ESP-controlled size specific emission factors, respectively. The use of such limited data results in questionable emission factors with which to characterize the industry's emissions.

E-rated cumulative size specific emission factors have been developed for uncontrolled and ESP-controlled emissions from reverberatory smelter operations and are presented in Table 23 and Figure 17. Only one set of C-quality cumulative particle size distribution data for uncontrolled emissions was combined with a B-rated particulate matter emission factor. Lower quality size distribution data was not considered. Two sets of C-quality cumulative particle size distribution data for ESP-controlled emissions were combined with an estimated particulate matter emission factor rating. The use of such limited data results in questionable emission factors with which to characterize the industry's emissions.

E-rated cumulative size specific emission factors have been developed for uncontrolled and ESP-controlled emissions from the copper converter process and are shown in Table 24 and Figure 18. Only one set of B-quality cumulative particle size distribution data for uncontrolled and controlled emissions were combined with a B-rated and an estimated particulate matter emissions factor, respectively. Lower quality size distribution data was not considered.

D-rated cumulative size specific emission factors have been developed for fugitive emissions from converter slag and copper blow operations and are shown in Table 25 and Figure 19. Three sets of A-quality cumulative particle size distribution data from the Playas, New Mexico facility of Phelps Dodge were combined with a B-rated particulate matter emission factor. Since the distribution data were only from one source, it is difficult to upgrade the D-rating of the cumulative size specific emission factor since it may not be represenatative of the industry at large. Additional data are desired.

3.3 CHEMICAL CHARACTERIZATION (Ref. 16)

The following subsection describes the chemical makeup of particulate matter emissions from primary copper production processes. Particulate

TABLE 18. FACTORS AND PARTICLE SIZE DISTRIBUTION FOR FUGITIVE EMISSIONS FROM REVERBERATORY FURNACE MATTE TAPPING OPERATIONS

EMISSION FACTOR RATING: D

Particle size (μm)	Cumulative mass % ≤ than stated size	Cumulative emission factors[a,b]	
		kg/Mg	lb/ton
	Uncontrolled	Uncontrolled	Uncontrolled
15	76	0.076	0.152
10	74	0.074	0.148
6	72.5	0.072	0.144
2.5	69.5	0.069	0.138
1.25	67.5	0.067	0.134
0.625	64	0.065	0.130
Total	100	0.100	0.200

[a] Expressed as units per unit weight of concentrated ore processed by the smelter.

[b] Reference 33.

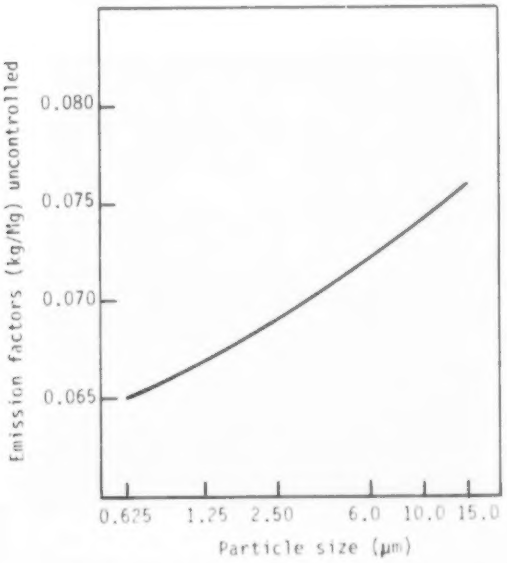

Figure 14. Cumulative emission factors less than stated particle size for fugitive emissions from reverberatory furnace matte tapping operations.

TABLE 19. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR FUGITIVE EMISSIONS FROM REVERBERATORY FURNACE SLAG TAPPING OPERATIONS

EMISSION FACTOR RATING: D

Particle size (μm)	Cumulative mass % ≤ than stated size	Cumulative emission factors[a,b]	
		kg/Mg	lb/ton
	Uncontrolled	Uncontrolled	Uncontrolled
15	33	0.033	0.066
10	28	0.028	0.056
6	25	0.025	0.050
2.5	22	0.022	0.044
1.25	20	0.020	0.040
0.625	17	0.017	0.034
Total	100	0.100	0.200

[a] Expressed as units per unit weight of concentrated ore processed by the smelter.

[b] Reference 33.

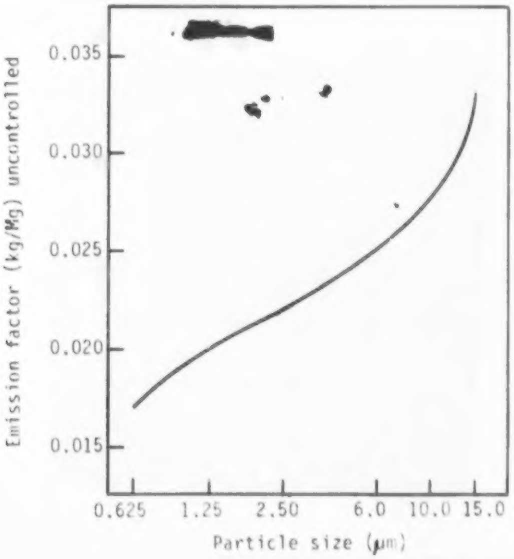

Figure 15. Cumulative emission factors less than stated particle size for fugitive emissions from reverberatory furnace matte slag tapping operations.

TABLE 20. EMISSION FACTORS FOR PRIMARY COPPER SMELTERS[a,b]

		Particulate matter		SO_2	
Smelter configuration[c]	Unit	lb/ton	kg/Mg	lb/ton	kg/Mg
Reverberatory furnace (RF) followed by converters (C)	RF	50	25	320	160
	C	36	18	740	370
Multiple hearth roaster (MHF) followed by reverberatory furnace (RF) and converters (C)	MHR	45	22	300	150
	RF	50	25	200	100
	C	36	18	660	330
Fluid bed roaster (FBR) followed by reverberatory furnace (RF) and converters (C)	FBR	NA	NA[d]	450	225
	RF	50	25	200	100
	C	36	18	660	330
Concentrate dryer (CD) followed by electric furnace (EF) and converters (C)	CD	10	5	1	0.5
	EF	100	50	240	120
	C	36	18	820	410
Fluid bed roaster (FBR) followed by electric furnace (EF) and converters (C)	FBR	NA	NA	450	225
	EF	100	50	92	46
	C	36	18	660	330
Concentrate dryer (DC) followed by flash furnace (FF), slag cleaning furnace (SS) and converters (C)	CD	10	5	1	0.5
	FF	140	70	920	460
	SS[e]	10	5	1	0.5
	C	NA[f]	NA[f]	274	137
Concentrate dryer (CD) followed by Noranda reactors (NR) and converters (C)	CD	10	5	1	0.5
	NR	NA	NA	NA	NA
	C	NA	NA	NA	NA

---

[a] Emission factors are expressed as units per unit weight of concentrated ore processed by the smelter. Approximately four unit weights of concentrate are required per unit weight of copper produced.

[b] Reference 41.

[c] In addition to the emission sources indicated, each smelter configuration contains fire-refining anode furnaces which follow the converters. The anode furnaces have negligible SO_2 emissions. No particulate emission data are available for anode furnaces.

[d] NA -- Not available.

[e] Slag cleaning furnace is used to recover copper from furnace slag and converter slag.

[f] Since the converters at flash furnace smelters treat high copper content matte, the converter cycle length is usually shorter than the converter cycle length at conventional smelters. Therefore, the converter particulate emissions from flash furnace smelters can be expected to be lower than the corresponding emissions from conventional smelters.

TABLE 21. FUGITIVE EMISSION FACTORS FOR PRIMARY COPPER SMELTERS[a]

EMISSION FACTOR RATING: B

Source of emission	Particulate matter kg/Mg	Particulate matter lb/ton	SO_2 kg/Mg	SO_2 lb/ton
Roaster calcine discharge	1.3	2.6	0.5	1
Smelting furnace[b]	0.2	0.4	2	4
Converters	2.2	4.4	65	130
Converter slag return	NA	NA	0.05	0.1
Anode furnace	0.25	0.5	0.05	0.1
Slag cleaning furnace[c]	4	8	3	6

[a] References 16, 22, 24 to 26. Expressed as mass units per unit weight of concentrated ore processed by the smelter. Approximately 4 unit weights of concentrate are required to produce 1 unit weight of copper metal. Factors for flash furnace smelters and Noranda furnace smelters may be slightly lower than reported values. NA = not available.

[b] Includes fugitive emissions from matte tapping and slag skimming operations. About 50 percent of fugitive particulate matter emissions and about 90 percent of total SO_2 emissions are from matte tapping operations. The remainder is from slag skimming.

[c] Used to treat slags from smelting furnaces and converters at the flash furnace smelter.

TABLE 22. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSIONS FROM MULTIPLE HEARTH ROASTER AND REVERBERATORY SMELTER OPERATIONS

EMISSION FACTOR RATING: D (UNCONTROLLED)
D (ESP CONTROLLED)

Particle size[b] (µm)	Cumulative mass % ≤ stated size		Cumulative emission factors			
			Uncontrolled		ESP controlled[c]	
	Uncontrolled	ESP controlled	kg/Mg	lb/ton	kg/Mg	lb/ton
15	100	100	47	95	0.47	0.95
10	100	99	47	94	0.47	0.94
5	100	98	47	93	0.46	0.93
2.5	97	84	46	80	0.40	0.80
1.25	66	76	31	72	0.36	0.72
0.625	25	62	12	59	0.29	0.59
Total	100	100	47	95	0.47	0.95

[a] Reference 36. Expressed as units per unit weight of concentrated ore processed by the smelter.

[b] Expressed as aerodynamic equivalent diameter.

[c] Nominal particulate removal efficiency of 99 percent.

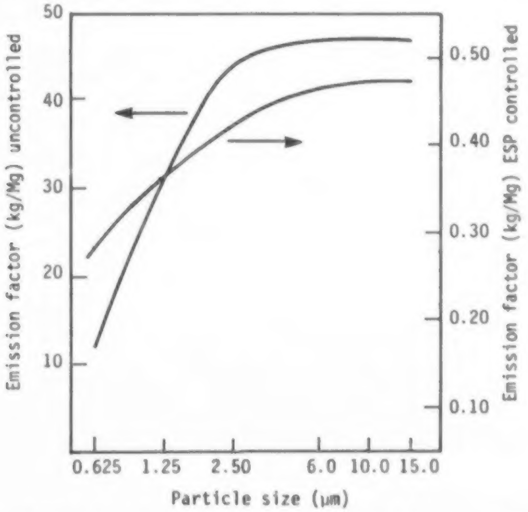

Figure 16. Cumulative size specific emission factors for emissions from multiple hearth roaster and reverberatory smelter

TABLE 23. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSIONS FROM REVERBERATORY SMELTER OPERATIONS[a]

EMISSION FACTOR RATING: E (UNCONTROLLED)
E (ESP CONTROLLED)

Particle size[b] (µm)	Cumulative mass % ≤ stated size		Cumulative emission factors			
			Uncontrolled		ESP controlled[c]	
	Uncontrolled	ESP controlled	kg/Mg	lb/ton	kg/Mg	lb/ton
15	NR[d]	83	NR	NR	0.21	0.42
10	27	78	6.8	13.6	0.20	0.40
5	23	69	5.8	11.6	0.18	0.36
2.5	21	56	5.3	10.6	0.14	0.23
1.25	16	40	4.0	8.0	0.10	0.20
0.625	9	32	2.3	4.6	0.08	0.16
Total	100	100	25	50	0.25	0.50

[a] Reference 39. Expressed as units per unit weight of concentrated ore processed by the smelter.
[b] Expressed as aerodynamic equivalent diameter.
[c] Nominal paritculate removal efficiency of 99 percent.
[d] NR -- Not reported due to excessive extrapolation.

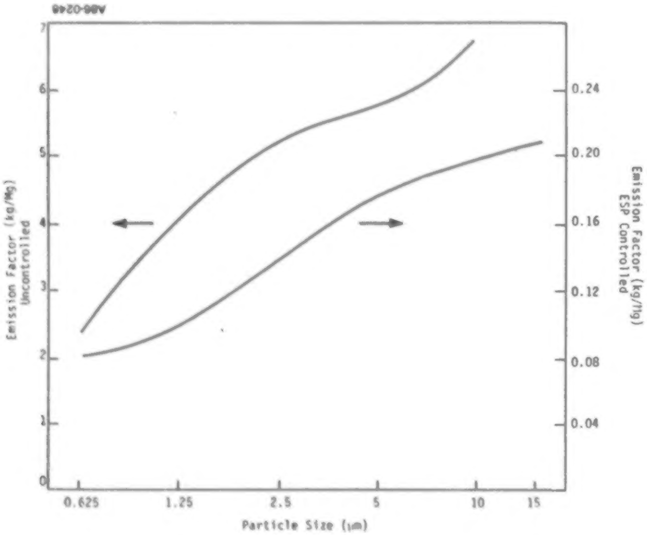

Figure 17. Cumulative size specific emission factors for emissions from reverberatory smelting

TABLE 24. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSIONS FROM COPPER CONVERTER OPERATIONS[a]

EMISSION FACTOR RATING: E (UNCONTROLLED)
E (ESP CONTROLLED)

Particle size[b] (µm)	Cumulative mass % ≤ stated size		Cumulative emission factors			
			Uncontrolled		ESP controlled[c]	
	Uncontrolled	ESP controlled	kg/Mg	lb/ton	kg/Mg	lb/ton
15	NR[d]	100	NR	NR	0.18	0.36
10	59	99	10.6	21.2	0.17	0.36
5	32	72	5.8	11.5	0.13	0.26
2.5	12	56	2.2	4.3	0.10	0.20
1.25	3	42	0.5	1.1	0.08	0.15
0.625	1	30	0.2	0.4	0.05	0.11
Total	100	100	18	36	0.18	0.36

[a] Reference 36. Expressed as units per unit weight of concentrated ore processed by the smelter.

[b] Expressed as aerodynamic equivalent diameter.

[c] Nominal particulate removal efficiency of 99 percent.

[d] NR -- Not reported due to excessive extrapolation.

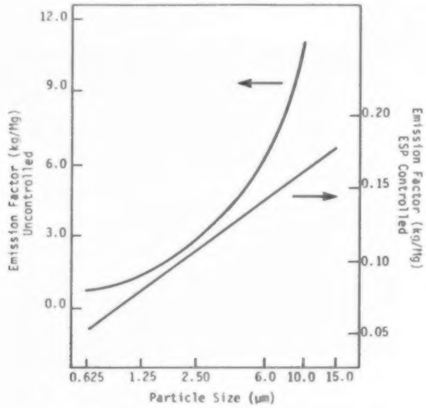

Figure 18. Cumulative size specific emission factors for emissions from copper converting.

TABLE 25. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR FUGITIVE EMISSIONS FROM CONVERTER SLAG AND COPPER BLOW OPERATIONS[a]

EMISSION FACTOR RATING: D

Particle size[b] (µm)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
	Uncontrolled	Uncontrolled	Uncontrolled
15	98	2.2	4.3
10	96	2.1	4.2
5	87	1.9	3.8
2.5	60	1.3	2.6
1.25	47	1.0	2.1
0.625	38	0.8	1.7
Total	100	2.2	4.4

[a] Reference 35. Expressed as units per unit weight of concentrated ore processed by the smelter.
[b] Expressed as aerodynamic equivalent diameter.

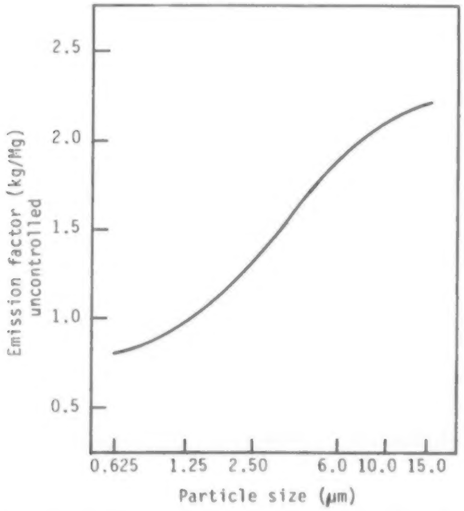

Figure 19. Cumulative size specific emission factors for fugitive emissions from converter slag and copper blow operations.

emissions from a multihearth roaster typically consist of large amounts of copper, iron metallic oxides and trace amounts of other constituents. Table 26 shows typcial concentrations of various components of the roaster particulate emissions (Ref. 42).

Particulate emissions from reverberatory furnaces consist of significant amounts of copper and lower amounts of other elements. One analysis of the particulates showed 24 percent copper and concentrations of other elements as shown in Table 27.

Other investigations indicate that most of the volatilized As, Se, Pb, Sb, Cd, Cr, and Zn emissions will be generated in the reverberatory furnace (Ref. 24, 36, and 43).

The results of the chemical analysis of particulate emissions from electric smelting would be expected to be about the same as those for reverberatory smelting, although the quantity of emissions is probably less (Ref. 16).

Particulate emissions composition for flash smelting is also expected to be similar to that for the reverberatory furnace, although emissions of volatile metals such as Pb and Zn tend to be lower since they are kept to a minimum in the concentrates in order to prevent plating within the flash chamber. No published analyses were available.

Converter dusts consist of large amounts of copper, iron, silica, sulfur, and oxides and smaller amounts of many other elements. Table 28 presents a typical range of compositions of converter dust (Ref. 16 and 43).

Other processes, including acid recovery, fire refining, melting, casting, and precious metals recovery contribute to particulate emissions, but analyses of the emissions from these sources were not available.

TABLE 26. WEIGHT ANALYSIS OF UNCONTROLLED PARTICULATE EMISSIONS FROM A MULTIPLE HEARTH COPPER ROASTER

Component	Percent weight
Entrained particles	
Cu	23.8 to 34.5
Fe	21.2 to 30.7
S	1.7 to 2.5
As	Trace
Sb	Trace
Pb	Trace
Zn	Trace
Sn	Trace
Cd	Trace
Ni	Trace
Mn	Trace
Se	Trace
SiO_2, CaO	10 to 15
O_2 (oxides)	13 to 19
Inerts	0.8
Sublime particles	
As_2O_3	Trace to 17
Sb_2O_3	Trace to 13
Inerts	Trace

TABLE 27. ANALYSIS OF PARTICULATES EMITTED FROM A REVERBERATORY FURNACE[a]

Element	ppm
Zinc	44,000
Cadmium	310
Manganese	100
Chromium	45
Nickel	35
Mercury	2.5

[a] Reference 42.

TABLE 28. WEIGHT ANALYSIS OF UNCONTROLLED PARTICULATE EMISSIONS FROM COPPER CONVERTER OPERATIONS

Component	Percent weight
Cu	10 to 19.0
Fe	10 to 20.0
Pb	0.83 to 2.5
Bi	0.61
F	Nil
Sb	Nil
As	0.04 to 0.6
Se	0.03 to 0.5
Si	5.0 to 15.0
Mg	0.57
Mo	0.08
Al	0.4 to 3.60
O_2	21.0
Cl	Nil
Te	0.005 to 0.01
S	12.0
Ca	1.0

SECTION 4

PRIMARY LEAD PROCESSING

4.1 PRIMARY LEAD PROCESSING INDUSTRY

The following section is a source category report for particulate matter emissions from the primary lead processing industry. The section includes a description of the primary lead industry and the various processes involved in primary lead production. Sources of particulate matter emissions from the lead production processes are discussed for each proccess, as is the type of particulate matter emission control equipment used by the industry. Information concerning particulate matter emission rates and associated particle size distributions for the lead production processes are summarized and reviewed. Size-specific emission factors are then developed from this data, and rated according to the criteria outlined in Section 1. Finally, a revised AP-42 section on the lead industry is included.

4.1.1 Overview

Lead is a highly versatile metal. Although its use has evolved dramatically over the centuries, lead consumption remains among the highest for nonferrous metals. Originally used for decorative purposes due to its noncorrosive and highly malleable nature, its present uses are dominated by its electrical and chemical properties in batteries and as a gasoline additive.

From a 1981 base, demand for lead is expected to increase at an annual rate of about 1.8 percent through 2000. The growth in lead use is contingent on the development of cost-competitive and reliable electric vehicles for general and new industrial uses, major power supply load-leveling applications, and continuing high growth for uninterrupted power supply systems (Ref. 44). Moderating effects on this projected growth are the current EPA regulations which reduce the use of lead additives in gasoline as an octane improver, together with a general concern over lead in the environment. All other uses are projected to remain level or experience moderate increases. These use changes represent some variations in the end-use pattern, which will be reflected in considerably less dissipation of the metal into the general environment and greater recycling by the secondary lead industry by the year 2080. Secondary lead is expected to supply about 60 percent of the total U.S. demand, as opposed to a little over 50 percent in 1983 (Ref. 45).

Primary smelting and refining of lead is currently conducted by three companies at six separate plants in the United States: ASARCO, Inc. (44 percent), St. Joe Minerals Corp. (34 percent), and a joint venture between AMAX and Homestake Mining (22 percent) (Ref. 46). A breakdown of the industry is shown in Table 29. Total annual capacity is 665,000 tons (595,000 Mg), down by 130,000 tons (118,000 Mg) (Ref. 46) since late 1981, when the combined lead and zinc smelter and refinery plant operated by Bunker Hill Co. in Kellogg, Idaho was shut down. Each of the three currently operating primary lead producers have combination smelter and refinery plants in Missouri. In addition to these three plants, ASARCO operates smelters in Montana and Texas serviced by a common refinery in Nebraska (Ref. 46).

Lead ores are mined at 25 sites in seven states in the United States, accounting for 15 percent of world lead production (Ref. 47). Of this 15 percent, 90 percent is produced in Missouri by eight individual mines, and another 8 percent is mined in Idaho (Ref. 47).

Lead ores are found primarily in the form of galena (lead sulfide-PbS) ranging from 3 to 8 percent lead. Common impurities are copper (Cu), iron (Fe), and zinc (Zn), with trace amounts of antimony (Sb), bismuth (Bi), tin (Sn), and precious metals. Except in the rich Missouri belt where lead concentrations are generally high, the recovered impurities in lead ores are often of greater value than the lead itself (Ref. 47). Prior to leaving the mine site, the ores are treated by a gravity separation process that produces a concentrate containing 55 to 70 percent lead and 13 to 19 percent sulfur (Ref. 48).

4.1.2 Primary Lead Smelting and Refining Process

The production of refined lead bullion is typical of the metals smelting industry. The ore is sintered to remove sulfur and produce a material amenable to blast furnace reduction. The blast furnace produces a crude lead bullion that is subsequently refined by a variety of processes to remove any undesirable impurities and produce the desired quality of lead product. In addition to these main operations, subsidiary operations recover valuable byproduct metals, primarily cadmium (Cd), Zn, Sb, and Bi. Figure 20 presents a simplified process flow diagram for lead smelting and refining.

The sintering of lead ore is a three-step process: (1) the ore concentrate is blended with sinter recycle material, fine dust, and sulfide-free fluxes used to maintain a 5 to 7 percent sulfur concentration in the sinter feed; (2) the ore blend is made into pellets 0.1 to 0.2 in. (3 to 5 mm) in diameter with the addition of a small percentage of water; and (3) the feed pellets are placed in direct contact with hot combustion gases, in either an updraft or downdraft sintering machine. Figure 21 shows the cross section of a typical updraft sintering machine.

The primary reactions involved in the sintering machine result in the oxidation of lead sulfide (PbS) producing lead oxide (PbO) and lead sulfate ($PbSO_4$):

TABLE 29. U.S. PRIMARY LEAD SMELTING AND REFINING CAPACITY (Ref. 46,47)

Producer	Plant location	Plant type	Annual capacity (tons)	Annual capacity (Mg)
AMAX and Homestake	Boss, Missouri	Smelter and refinery	140,000	127,000
ASARCO	El Paso, Texas	Smelter	90,000	82,000
ASARCO	East Helena, Montana	Smelter	90,000	82,000
ASARCO	Omaha, Nebraska	Refinery	180,000	164,000
ASARCO	Glover, Missouri	Smelter and refinery	110,000	100,000
St. Joe Minerals	Herculaneum, Missouri	Smelter and refinery	225,000	204,000
Total Smelting and Refining			665,000	595,000

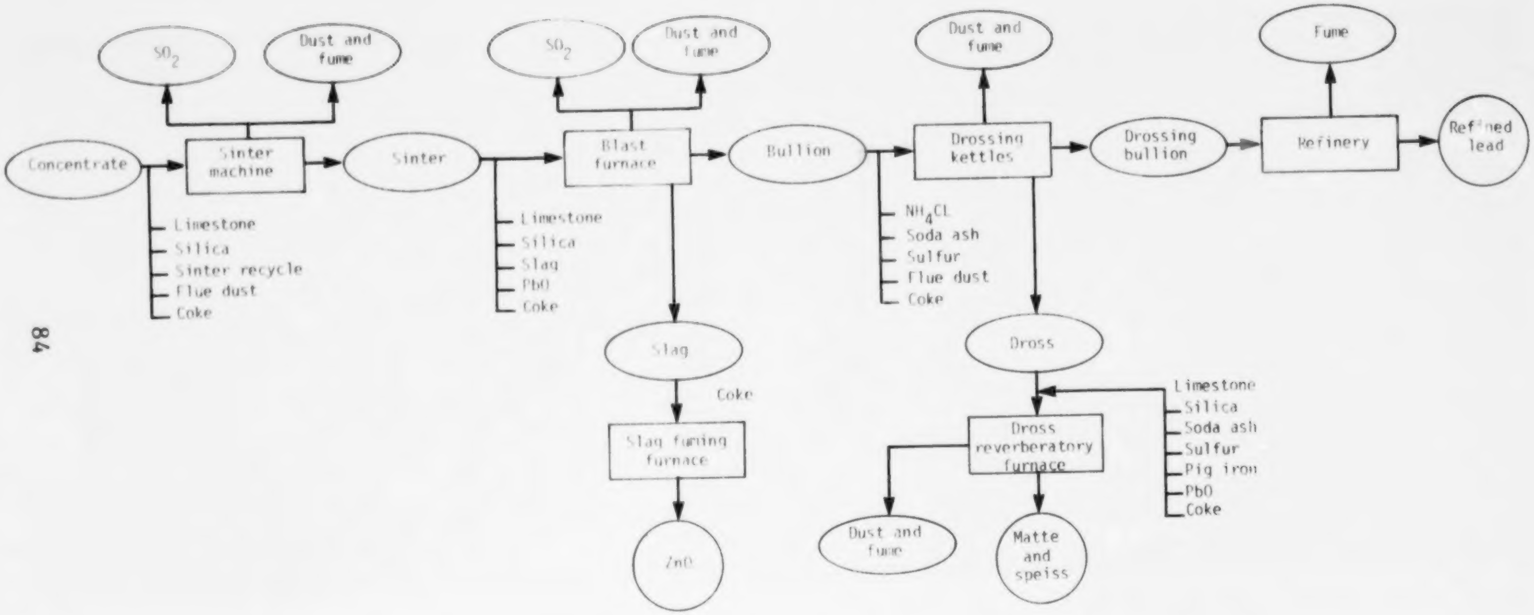
SO2
Dust and fume
Concentrate
Sinter machine
Limestone
Silica
Sinter recycle
Flue dust
Coke
Sinter
SO2
Dust and fume
Blast furnace
Limestone
Silica
Slag
PbO
Coke
Slag
Coke
Slag fuming furnace
ZnO
Bullion
NH4CL
Soda ash
Sulfur
Flue dust
Coke
Dust and fume
Drossing kettles
Dross
Limestone
Silica
Soda ash
Sulfur
Pig iron
PbO
Coke
Dross reverberatory furnace
Dust and fume
Matte and speiss
Drossing bullion
Fume
Refinery
Refined lead

Figure 20. Typical primary lead smelter process schematic (Ref. 48).

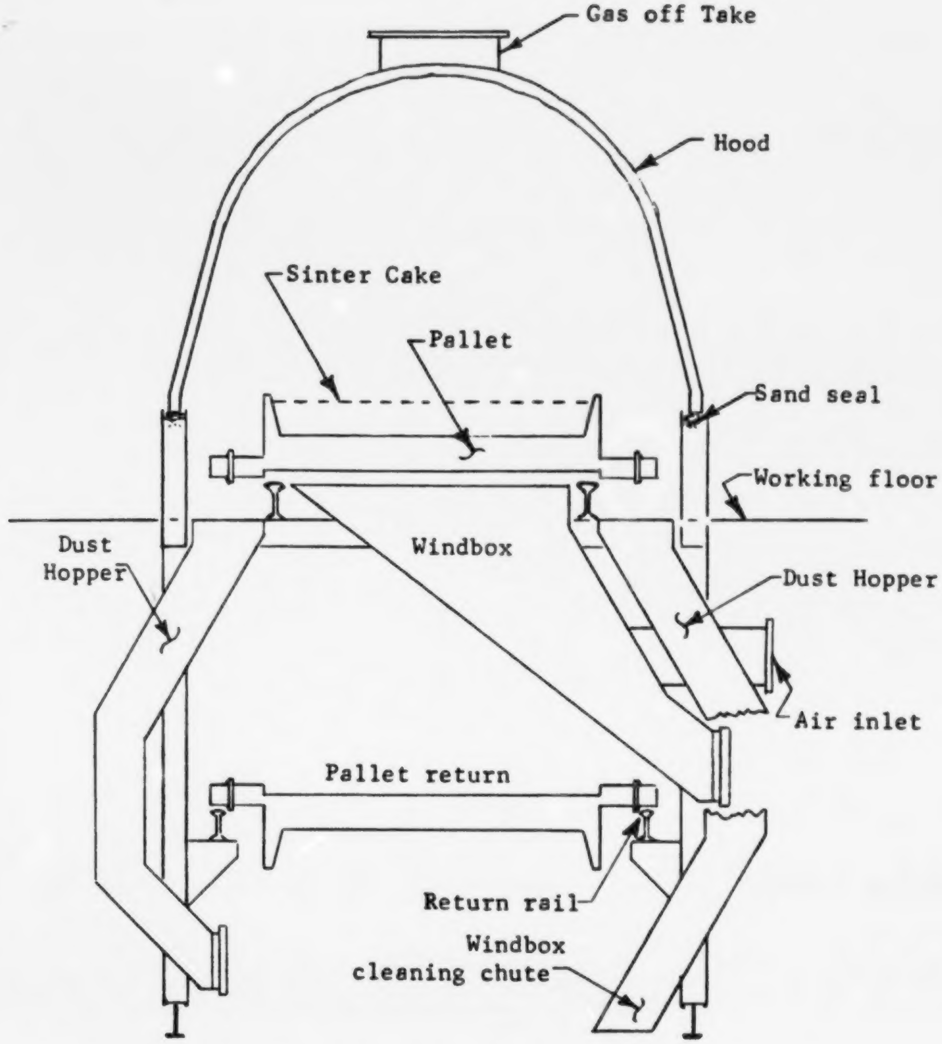
Gas off Take
Hood
Sinter Cake
Pallet
Sand seal
Working floor
Dust Hopper
Windbox
Dust Hopper
Air inlet
Pallet return
Return rail
Windbox cleaning chute

Figure 21. Lead updraft sinter machine (Ref. 49).

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \qquad (1)$$

$$PbS + 2O_2 \rightarrow PbSO_4 \qquad (2)$$

Secondary reactions forming the volatile oxides of arsenic and antimony also occur. Temperatures of approximately 1,800°F (980°C) are achieved in the sintering machine during the oxidation of both the lead sulfide in the source ore as well as the coke, oil, or gas fuel used to ignite the sinter feed. The porous sintered product, known as clinker, is then crushed in preparation for the blast furnace, while the fines produced (over one-third of the sinter product) are recycled through the sinter machine.

All but one of the smelting plants operating in the United States use updraft sintering machines, with ASARCO's El Paso, Texas smelter operating a downdraft sintering machine (Ref. 48). Since up to 20 percent of the sinter feed can be emitted as dust and metallic fume, solids recovery using either a baghouse or ESP is used at all sinter machines operating in the United States. These solids are typically recycled through the sintering machine. In addition to solids recovery, two of the five U.S. primary lead smelters have acid plants that treat the high SO_2 concentration gases produced by the sintering machine (Ref. 48).

The sinter product is fed to the blast furnace in combination with flux materials (slag, silica, and limestone) and metallurgical coke. Figure 22 presents a typical lead blast furnace. The furnace charge enters through water-cooled ports at the top of the furnace, and then settles out at the bottom. Air is injected through tuyeres located along the side of the furnace. This provides oxygen to burn the coke, thus generating the heat required to melt the lead produced. The primary reactions taking place in the blast furnace are as follows:

$$C + O_2 \rightarrow CO_2 \qquad (3)$$

$$C + CO_2 \rightarrow 2CO \qquad (4)$$

$$PbO + CO \rightarrow Pb + CO_2 \qquad (5)$$

Secondary reactions produce metallic lead from the lead sulfides and sulfates remaining in the sinter product.

$$2PbO + PbS \rightarrow 3Pb + SO_2 \qquad (6)$$

$$PbSO_4 + PbS \rightarrow 2Pb + 2SO_2 \qquad (7)$$

The net result of the blast furnace operation is the formation of as many as four separate layers. At the bottom lies molten lead bullion containing between 94 and 98 percent lead with the remainder made up of impurities such as Cu, Sb, arsenic (As), and Fe. Blast furnace feed containing substantial quantities of Sb and/or As will result in the formation of a speiss layer above the molten lead. This speiss layer

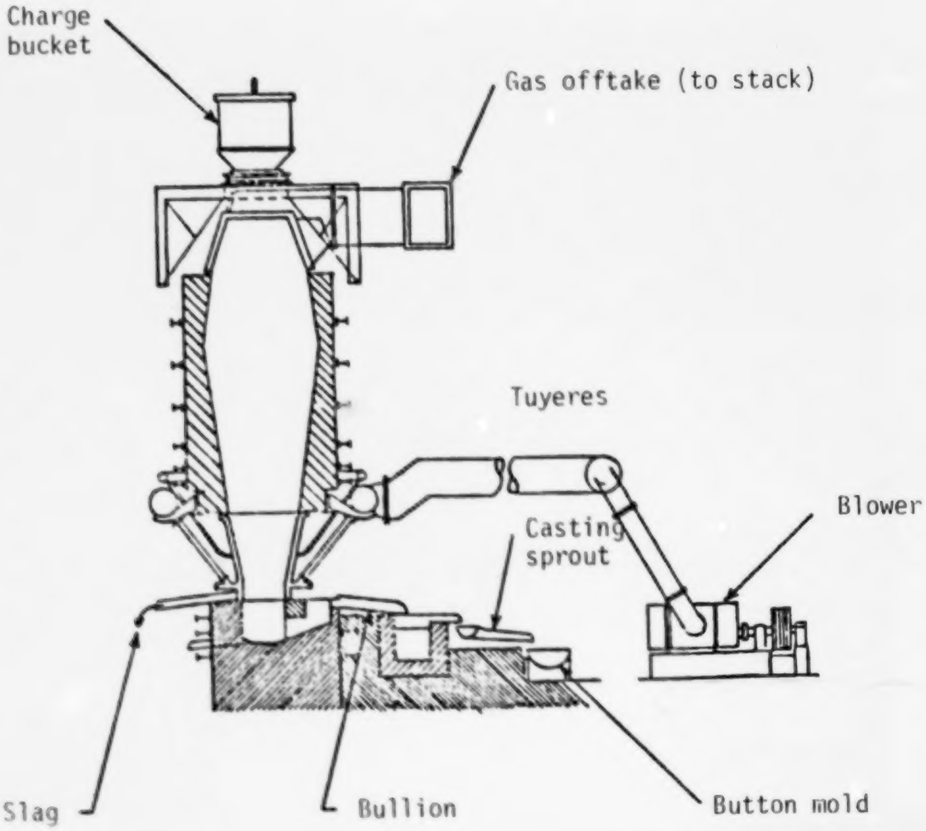
Charge bucket
Gas offtake (to stack)
Tuyeres
Blower
Casting sprout
Slag
Bullion
Button mold

Figure 22. Primary processing lead blast furnace (Ref. 50).

contains compounds of Fe and other metals with the Sb and As. Above this, an additional layer forms, comprised primarily of Cu with additional lead and S. This is known as matte. Slag containing iron and calcium silicates forms a crust above the other three layers. As in sintering operations, a significant portion of the blast furnace feed forms dust and metallic fume emissions. In all five U.S. smelters, baghouses are employed to control particulate emissions. The collected solids are then recycled to either the blast furnace or sintering machine.

The first step in the refining of the lead bullion produced by the blast furnace is the removal of Cu by drossing. The molten lead is placed in kettles, cooled to 700° to 900°F (370° to 480°C), and agitated with air lances. PbO, Cu and other materials insoluble at the reduced temperatures form a solid crust which is skimmed off the molten bullion. This usually accounts for 10 to 35 percent of the bullion feed (Ref. 47). Additional Cu removal can be achieved by adding elemental sulfur to the bullion which preferentially forms an insoluble Cu_2S dross. The reaction is:

$$2Cu + S \rightarrow Cu_2S \tag{8}$$

Particulates and metallic fumes released by the drossing kettles are significant and in all cases are combined with the blast furnace gases prior to solids recovery through a baghouse.

Since the dross contains up to 90 percent PbO, subsequent reduction in a dross reverberatory furnace is conducted to recover this lead, as well as producing further layers of matte and speiss. Figure 23 shows a lead reverberatory furnace and associated particulate controls.

The drossed bullion then undergoes any of a variety of refining steps to remove impurities found in the source ore. Softening by any of three separate techniques (reverberatory, kettle, or Harris softening) removes Sb. Zn is used to remove silver (Ag) using the Parkes desilverizing process. Zn is then removed using either the vacuum, chlorine, or Harris dezincing process. A final refining step is the removal of Bi.

4.1.3 Particulate Emission Sources

Particulate emissions are generated as part of the normal operation at a lead smelting and refining plant. Particulates are emitted during raw material handling, smelting, refining, and product handling. A process flow diagram for a typical lead smelter and refinery facility showing particulate emission sources is presented in Figure 20.

Fugitive emissions result primarily from materials storage, crushing, and transfer operations. Smelter feed materials release particulate emissions during unloading and storage. Sinter feed preparation, which includes crushing, mixing, and pelletization, are further sources of fugitive particulate emissions. Sinter crushing and blast furnace feed preparation produce additional particulates. Blast furnace tapping, ladling into kettles, and final casting are also sources of fugitive emissions.

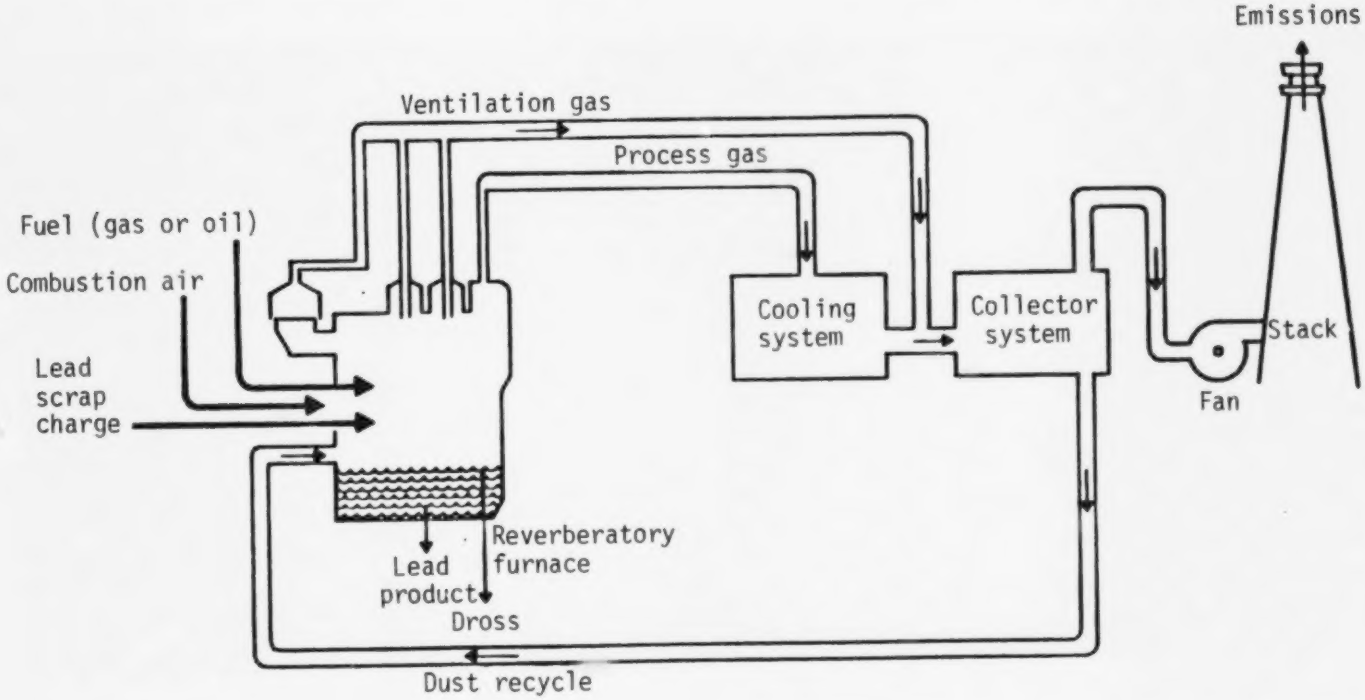
Emissions
Ventilation gas
Process gas
Fuel (gas or oil)
Combustion air
Lead scrap charge
Cooling system
Collector system
Stack
Fan
Reverberatory furnace
Lead product
Dross
Dust recycle

Figure 23. Primary processing lead reverberatory furnace (Ref. 51).

The particulate emission rates from fugitive sources are dependent on a variety of operational conditions. Excessive fugitive emissions can result due to improper maintenance of equipment as well as plant operation in excess of design conditions.

Principal point sources of particulate emissions are sinter machines and blast furnaces. Additional sources include slag fuming and dross reverberatory furnaces if the plant has these facilities. Excessive emission rates can result from improper maintenance of equipment as well as plant operation in excess of design conditions.

Blast furnaces experience especially high emission rates during furnace blows. A blow occurs when material builds up on the sides of the furnace, forming a chimney. When such a chimney has formed, the blast furnace feed air moves directly through the furnace without achieving optimal contact with the furnace charge material. The actual blow occurs when the chimney collapses, resulting in extremely high particulate emission rates. Dynamiting of the blast furnace is a common method employed to reduce the possibility of a blow. This optimizes the reduction process as well as reducing the overall particulate emission rates.

4.1.4 Particulate Emission Controls (Ref. 52)

Various control techniques are used to reduce particulate emissions from primary lead smelting facilities. Many of these are integral to the plant operation and recover valuable material. Fugitive emissions are generally less significant and are controlled primarily to satisfy regulatory requirements.

Fugitive emissions generated by raw material handling and storage are controlled by the use of enclosures to shield storage areas from direct exposure to the wind. Water spraying is also used to reduce dust emissions from storage piles. Fugitive emissions from crushing, mixing, and transferring operations are generally controlled by baghouses, if at all. Ventilation air from within the buildings containing these facilities is either ducted to dedicated baghouses or added to flue gases from the sinter machine or blast furnace.

Emissions from sinter machines are controlled using a variety of techniques. Some form of sulfur control is often practiced. An acid plant can be used to treat strong and weak SO_2 concentration effluent gases for the production of sulfuric acid, or a scrubber can remove the SO_2 from the sintering process exhaust gas. Particulates are usually controlled using a combination of water spraying, which also cools the flue gases and removes some particulate material, and a baghouse or ESP. The particulate control equipment can either be dedicated or serve the combined effluents of both the sinter machine and blast furnace.

Particulate emissions from blast furnaces are controlled primarily through the use of baghouses. In some plants, ventilation air and flue gases from auxiliary facilities such as the dross reverberatory furnace are ducted through the blast furnace baghouse. Water spray chambers are also used in some facilities prior to the baghouse to cool effluent gases so as not to damage baghouse filters. In facilities that have slag fuming furnaces where ZnO is recovered directly from the fume produced, a baghouse is typically used.

4.2 PRIMARY LEAD PROCESSING EMISSION FACTORS

4.2.1 Data Review

Total and size-specific particulate emissions data have been obtained from 12 emission tests at primary lead smelter and refinery plants. A summary of these tests, showing test site, emission source, emission type, control device, type of data obtained, when the test was conducted, and the quality of the data is summarized in Table 30 and shown graphically in Figures 24 through 29.

Total particulate emissions data referenced in the previous AP-42 Section were not reviewed. New data for sinter machine and blast furnace point source emissions were reviewed, and are reported in Table 31. Previous AP-42 data for fugitive emissions were obtained from a primary lead smelting and refining plant that is no longer operating. These data were therefore replaced by data from currently operating facilities, and are reported in Table 32.

Size-specific emissions data were obtained for both point and fugitive emission sources, and are reported in Table 33. Point source size distribution data were obtained for controlled blast furnace emissions from a single plant. Fugitive emission size distribution data were obtained from the ore storage area, sinter machine, blast furnace, dross kettle,and reverberatory furnace.

ASARCO: Glover (1973) (Tests 1 Through 5)

A total of 22 particulate sampling tests were conducted at five sites during the July 1973 testing at ASARCO's primary lead smelter in Glover, Missouri (Ref. 53). Of these, 17 were considered usable in this current study. Testing at this plant was conducted at both the sintering machine and blast furnace. Mass emission factor data from this source are presented in Table 31. Size distribution data from this source are presented in Table 33.

Particle sizing data were collected using an eight-stage (with backup filter) Andersen cascade impactor with an EPA Method 5 sampling train (RAC Model 2343 Stacksampler). Collection masses at each stage were reported. Size-specific emission factors could therefore be directly calculated from complementary mass emission factors determined from the same emission source.

Total particulate emission rate data were collected from all but one emission source using an EPA Method 5 sampling train (RAC Model 2343

TABLE 30. SUMMARY OF PARTICULATE EMISSIONS TESTS PRIMARY LEAD PROCESSING

Test no.	Source, location	Emission point	Emission type	Control device(s)	Type of data[a]	Test date	Test rating	Reference
1	ASARCO, Glover	Sinter machine process flue	Point source	--	2	July 1973	A	53
2	ASARCO, Glover	Sinter machine ventilation gases	Point source	--	2	July 1973	A	53
3	ASARCO, Glover	Sinter machine	Point source	Baghouse	2	July 1973	D	53
4	ASARCO, Glover	Blast furnace	Point source	--	2	July 1973	A	53
5	ASARCO, Glover	Blast furnace	Point source	Baghouse	1, 2	July 1973	A, A	53
6	ASARCO, Glover	Ore storage bin	Fugitive	--	1, 2	July 1976	B, A	54
7	ASARCO, Glover	Sinter building	Fugitive	--	1, 2	July 1976	B, A	54
8	ASARCO, Glover	Blast furnace	Fugitive	--	1, 2	July 1976	B, A	54
9	ASARCO, East Helena	Sinter building	Fugitive	--	1, 2	July 1976	B, A	54
10	ASARCO, East Helena	Blast furnace	Fugitive	--	1, 2	July 1976	B, A	54
11	ASARCO, East Helena	Dross kettle	Fugitive	--	1, 2	July 1976	B, A	54
12	ASARCO, East Helena	Reverberatory furnace	Fugitive	--	1, 2	July 1976	B, A	54

[a] 1 = Particle size distribution.
2 = Total particulate.

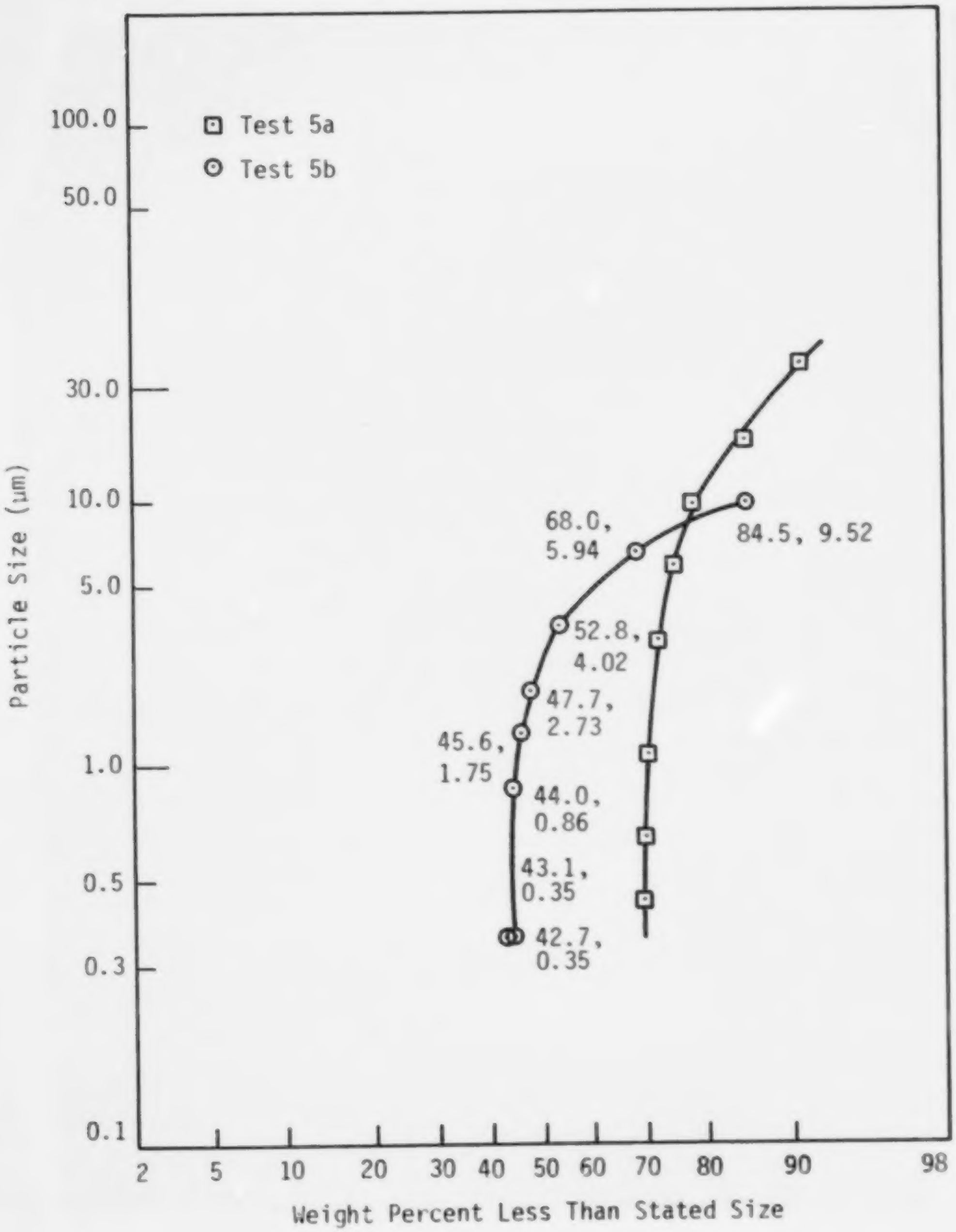

Figure 24. A-rated particle size distribution for controlled primary lead processing blast furnace flue gases.

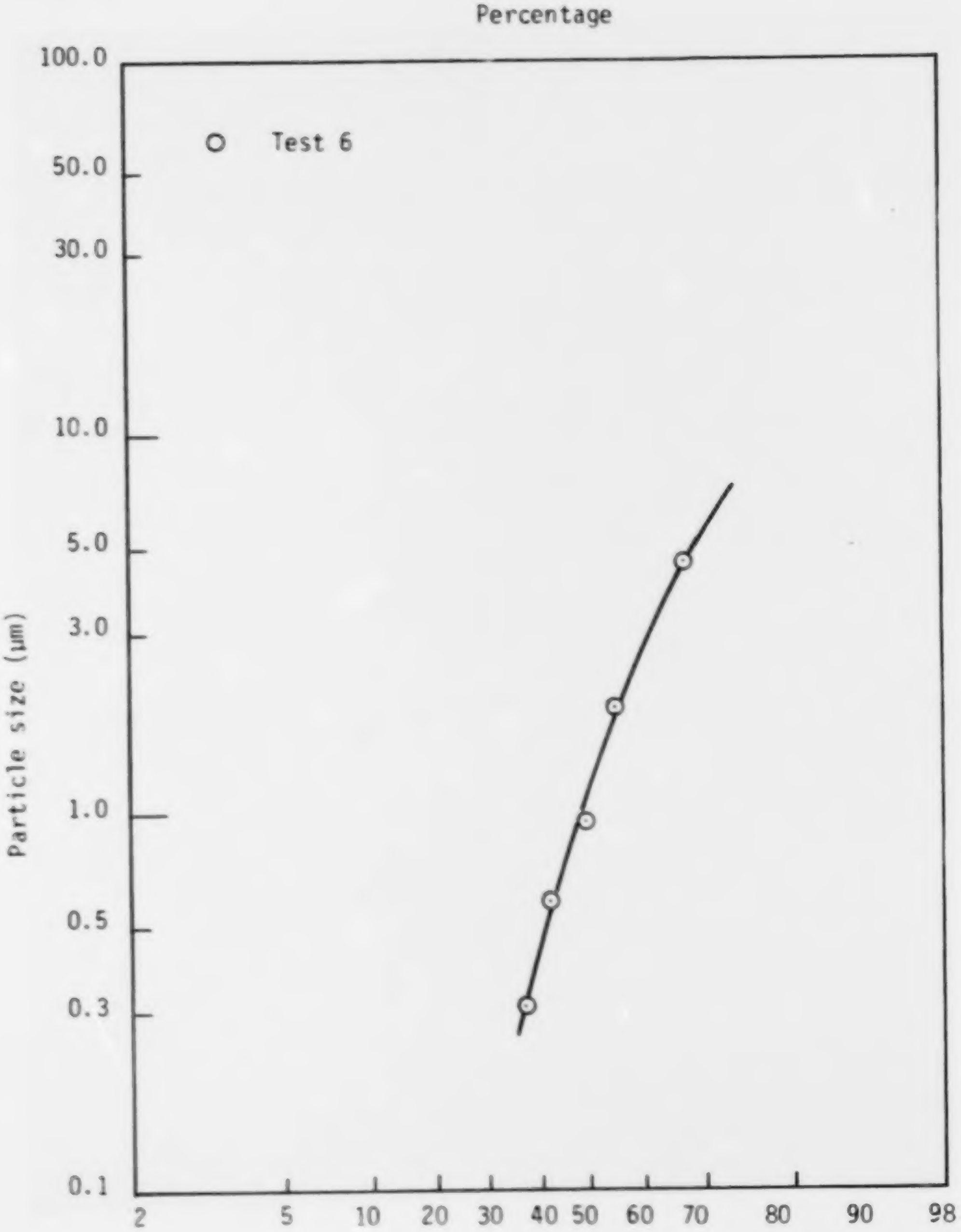

Figure 25. B-rated particle size distribution for fugitive emissions from primary lead processing ore storage.

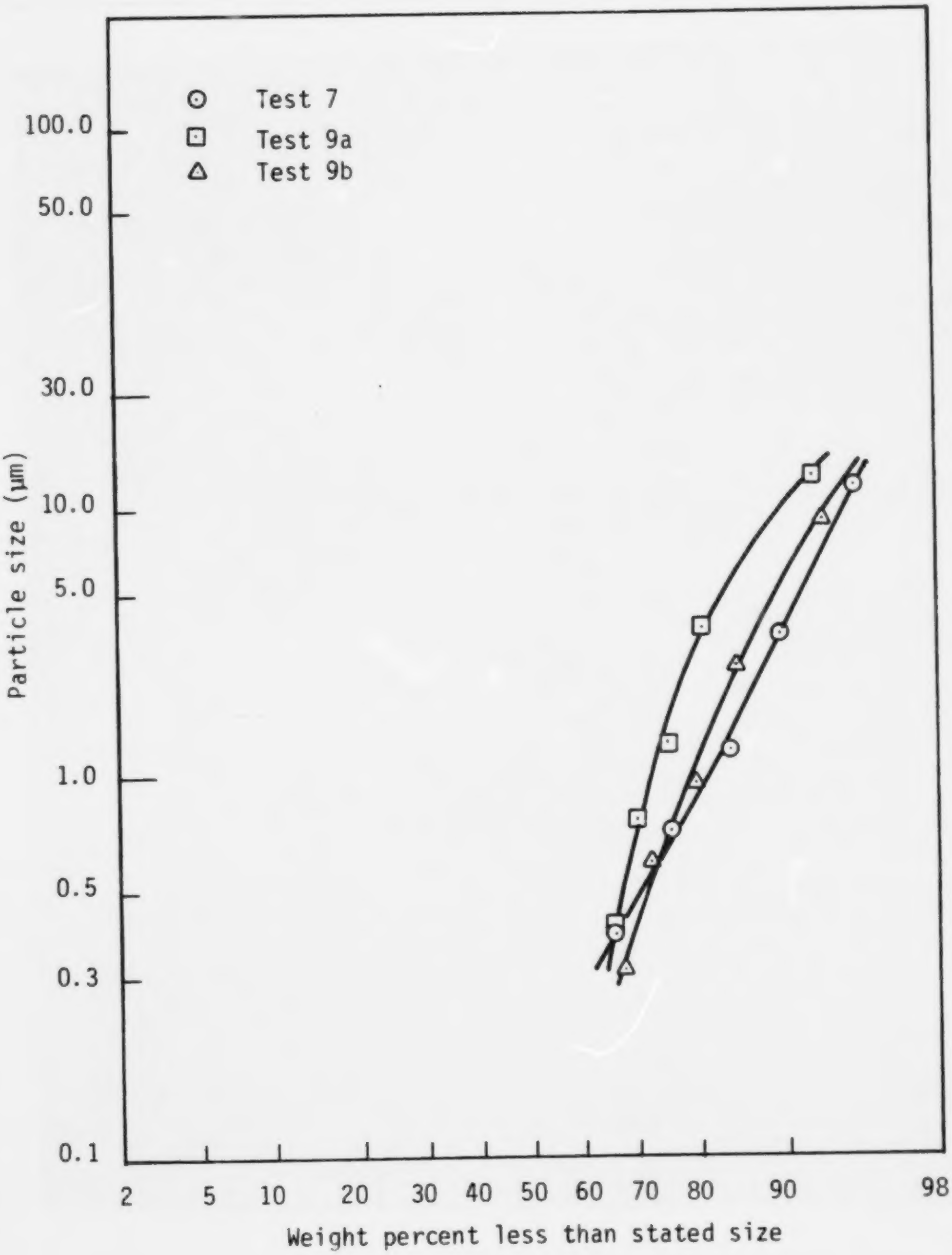

Figure 26. B-rated particle size distribution for fugitive emissions from a primary lead processing sinter machine.

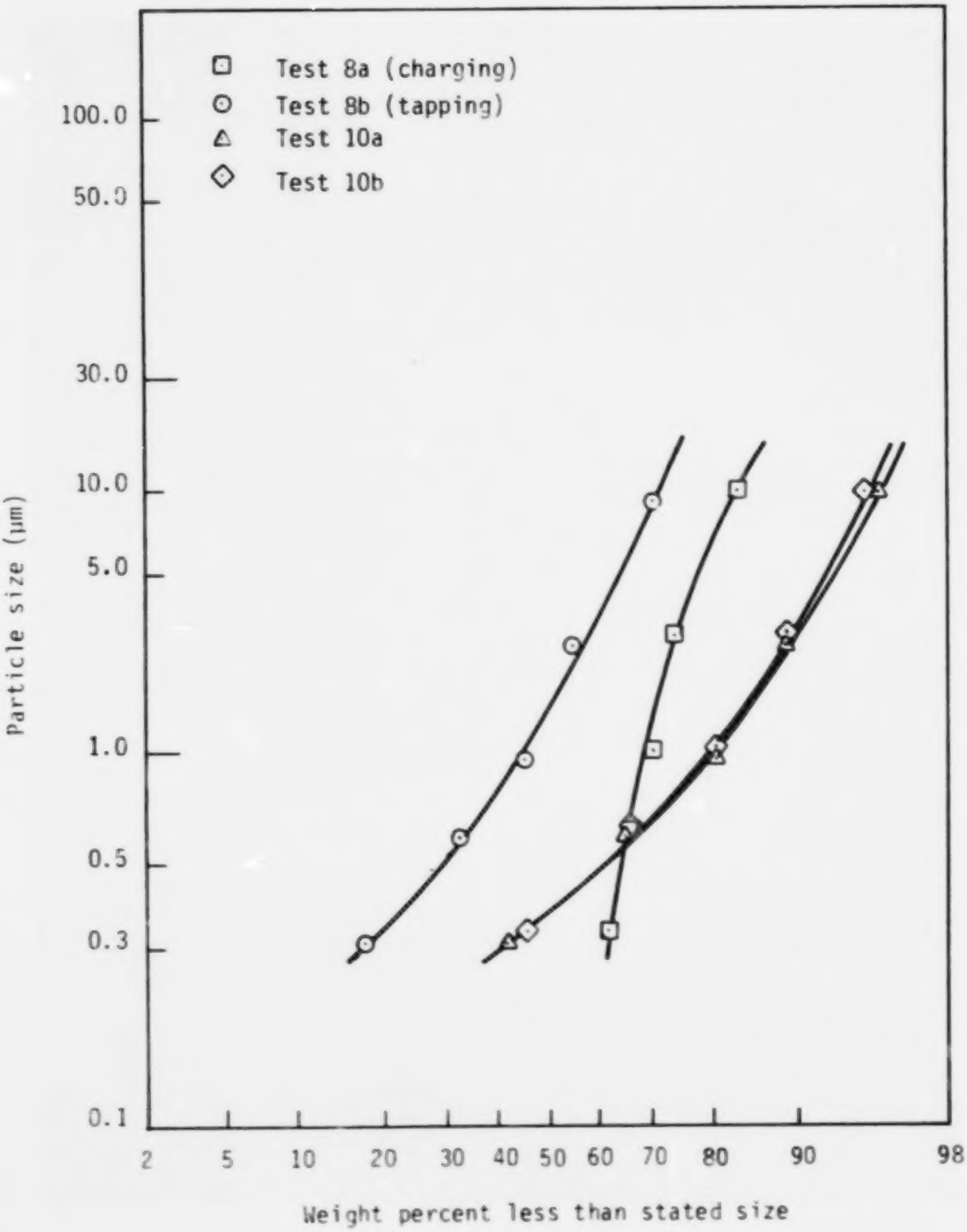

Figure 27. B-rated particle size distribution for fugitive emissions from a primary lead processing blast furnace.

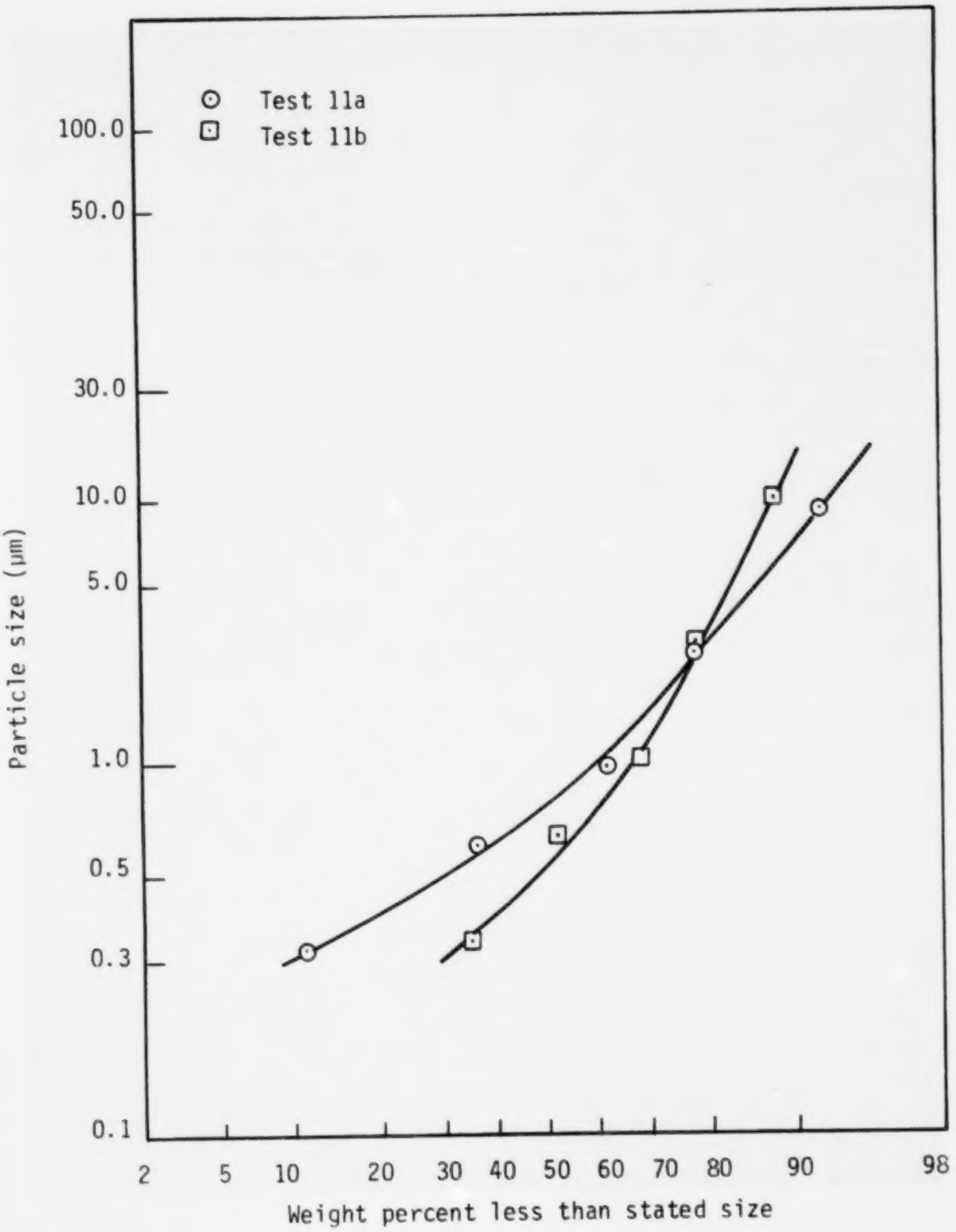

Figure 28. B-rated particle size distribution for fugitive emissions from a primary lead smelting dross kettle.

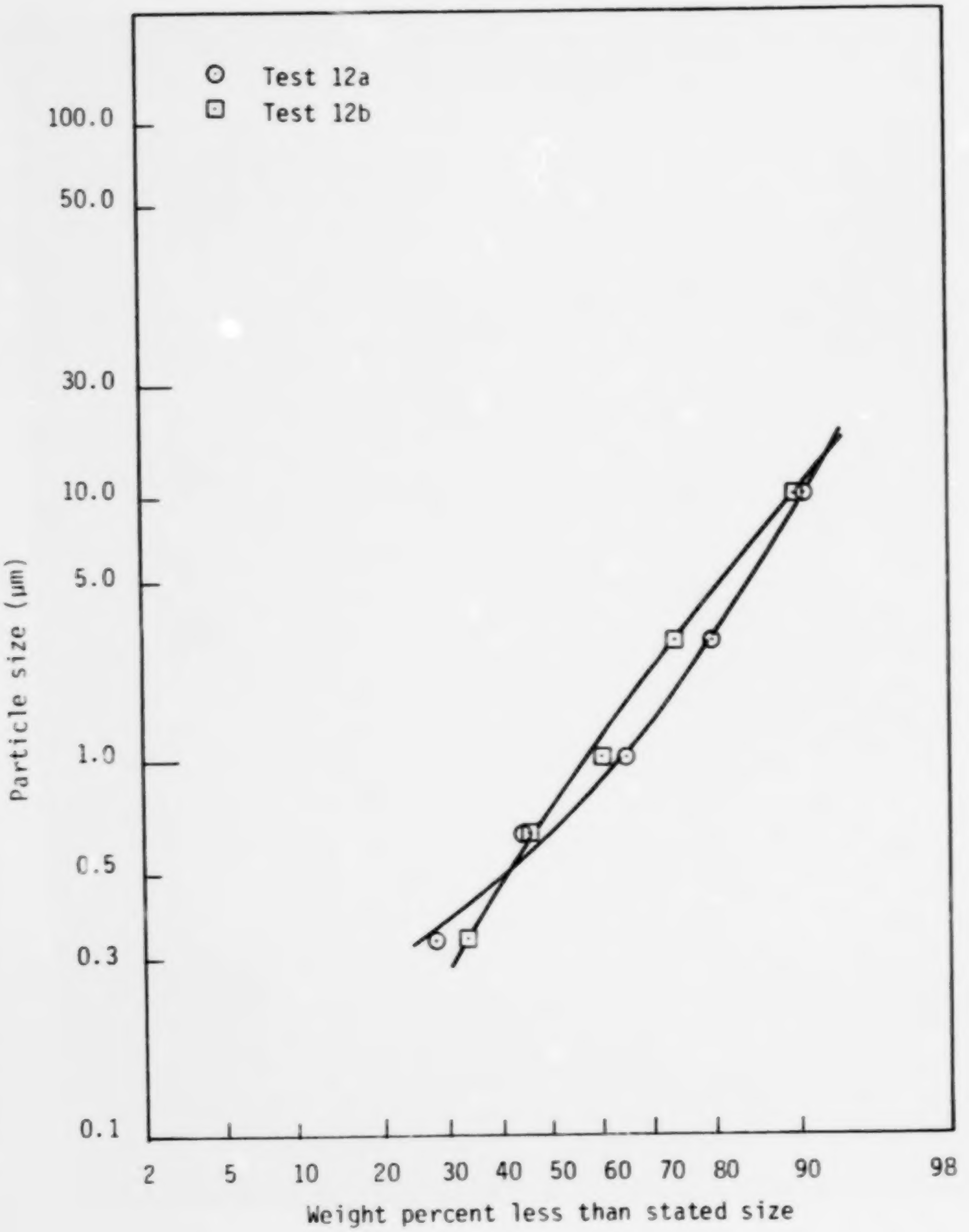

Figure 29. B-rated particle size distribution for fugitive emissions from a primary lead processing reverberatory furnace.

TABLE 31. POINT SOURCE PARTICULATE EMISSION RATE TEST DATA PRIMARY LEAD PROCESSING[a]

Test number	Production rate (ton/hr)	Emission rate (lb/hr)	Emission factor[b] (lb/ton)	Emission factor[b] (kg/Mg)	Emission test rating
Uncontrolled sinter machine emissions					
Process flue					
1^a	22.5	2,060	91.6	45.8	A
1^b	27.0	1,810	67.0	33.5	A
1^c	28.5	2,450	86.0	43.0	A
Ventilation gases					
2^a	27.7	1,360	49.1	24.5	A
2^b	22.6	1,090	48.2	24.1	A
2^c	27.0	852	31.6	15.8	A
Controlled sinter machine emissions					
3	24.6	4.94	0.20	0.10	D
Uncontrolled blast furnace emissions					
4^a	13.8	2,530	183.0	92.0	A
4^b	13.8	1,990	144.0	72.0	A
Controlled blast furnace emissions					
5^a	13.8	24.2	1.76	0.88	A
5^b	13.8	41.7	3.02	1.51	A

---

[a] Only new data, previously unreferenced in AP-42 are included. All data, from Reference 53.

[b] All emission factors are based on quantity of lead produced.

[c] Combination of three tests on each of three effluent streams from blast furnace baghouse, Reference 53.

TABLE 32. FUGITIVE PARTICULATE EMISSION RATE TEST DATA PRIMARY LEAD PROCESSING[a]

Test number	Production rate (ton/hr)	Emission rate (lb/hr)	Emission factor[b]		Emission factor rating
			(lb/ton)	(kg/Mb)	
Ore storage emissions					
6	13.8[b]	0.34	0.025	0.012	B
Sinter machine building emissions					
7	26.5[c]	5.07	0.19	0.10	B
9	15.0[d]	2.7	0.18	0.09	B
Blast furnace emissions					
8	13.8[c]	5.13	0.37	0.19	B
10	15.0[d]	1.46	0.10	0.05	B
Dross kettle emissions					
11	15.0[d]	5.4	0.36	0.18	B
Reverberatory furnace emissions					
12	15.0[d]	7.3	0.49	0.24	B

All data Reference 54.

[a] All emission factors are based on quantity of lead produced.

[b] Estimated from process rate data of rate limiting process from previous testing at same plant.

[c] Estimated from process rate data from previous testing at same plant.

[d] Estimated from process rate data of rate limiting process from previous testing at similar plant using production rates prorated on the basis of annual plant capacity.

TABLE 33. SUMMARY OF A-RATED DATA

Plant	Emission source	Total particulate (lb/ton Pb)	Run	Particulate size distribution										Data Rating	Reference
ASARCO Glover	Blast furnace (controlled)	1.76 3.02	5a	d_{50} (µm)	0.44	0.65	1.06	2.13	3.32	4.88	7.20	11.54	--	A	53
				Cum % <d_{50}	69.8	69.8	70.3	72.1	74.4	77.4	84.7	90.3	94.6		
			5b	d_{50} (µm)	0.35	0.53	0.86	1.75	2.73	4.02	5.94	9.52	--	A	53
				Cum % <d_{50}	42.7	43.1	44.0	45.6	47.7	52.8	68.0	84.5	94.4		
ASARCO Glover	Fugitive (storage bins)	0.025	6	d_{50} (µm)	0.31	0.59	0.95	1.9	4.6					B	54
				Cum % <d_{50}	48.0	52.8	59.8	65.6	77.2						
ASARCO Glover East Helena	Fugitive (sinter building)	0.19 0.18	7	d_{50} (µm)	0.38	0.71	1.15	2.1	5.6					B	54
				Cum % <d_{50}	66.2	75.8	83.9	89.1	94.6						
			9a	d_{50} (µm)	0.40	0.76	1.2	2.4	5.9					B	54
				Cum % <d_{50}	65.7	70.1	75.1	80.2	92.1						
			9b	d_{50} (µm)	0.31	0.59	0.95	1.9	4.6					B	54
				Cum % <d_{50}	67.8	72.8	79.1	84.5	92.7						

(Continued)

TABLE 33. (continued)

Plant	Emission source	Total particulate (lb/ton Pb)	Run	Particulate size distribution						Data Rating	Reference
ASARCO East Helena	Fugitive (blast furnace)	0.37 0.10	8a	d_{50} (µm)	0.33	0.63	1.0	2.03	4.9	B	54
				Cum % $<d_{50}$	62.6	66.4	70.4	74.6	83.7		
			8b	d_{50} (µm)	0.31	0.59	0.95	1.9	4.6	B	54
				Cum % $<d_{50}$	17.2	32.4	45.1	54.8	70.5		
			10a	d_{50} (µm)	0.31	0.59	0.95	1.9	4.6	B	54
				Cum % $<d_{50}$	41.4	65.2	80.6	89.0	95.5		
			10b	d_{50} (µm)	0.33	0.63	1.0	2.03	4.9	B	54
				Cum % $<d_{50}$	45.5	66.3	80.8	89.0	94.9		
ASARCO East Helena	Fugitive (dross kettle)	0.36	11a	d_{50} (µm)	0.31	0.59	0.95	1.9	4.6	B	54
				Cum % $<d_{50}$	11.8	37.4	63.6	78.4	92.4		
			11b	d_{50} (µm)	0.33	0.63	1.0	2.03	4.9	B	54
				Cum % $<d_{50}$	36.4	53.8	69.8	78.9	88.6		
ASARCO East Helena	Fugitive (reverberatory)	0.49	12a	d_{50} (µm)	0.33	0.63	1.0	2.03	4.9	B	54
				Cum % $<d_{50}$	29.0	45.4	66.1	80.1	90.8		
			12b	d_{50} (µm)	0.33	0.63	1.0	2.03	4.9	B	54
				Cum % $<d_{50}$	34.2	46.7	61.3	74.5	89.9		

Stacksampler). Controlled emissions from the sinter machine were sampled using an ASARCO installed "Askania" filter bag sampler since inadequate space existed in the breeching between the baghouse and the stack. Lead content was determined by atomic absorption spectrophotometry.

Seven particulate mass emission rate tests were conducted at the sinter machine. Three tests were conducted on the sinter machine process flue (test 1); three were conducted on the sinter-associated ventilation gases (test 2); a final test was conducted on the exit from the baghouse servicing the two previously referenced gas streams (test 3). For tests 1 and 2, standard EPA sampling techniques were used, and process rate data could be estimated from data provided. The lead production rate was estimated by subtracting the lead lost through emissions from the lead input rate.

$$\begin{array}{c} \text{production} \\ \text{rate} \end{array} = \begin{array}{c} \text{input feed} \\ \text{rate} \end{array} \times \begin{array}{c} \text{input feed} \\ \text{lead content} \end{array} - \begin{array}{c} \text{emission} \\ \text{rate} \end{array} \times \begin{array}{c} \text{emissions} \\ \text{lead content} \end{array}$$

Specific data for each test were provided to allow the calculation of the effective production rate. Tests 1 and 2 were therefore designated A-rated data. Test 3, however, was conducted using the "Askania" sampler installed by ASARCO. Since this is a nonstandard sampling technique, the test data were designated C-rated. The production rate during this test was estimated using the technique previously described. No particle sizing data were obtained for the sinter machine emissions.

Twelve particulate mass emission rate tests were conducted at ASARCO's Glover, Missouri blast furnace on both controlled and uncontrolled emissions. Test 4 was a series of three runs on the exhaust flue prior to the blast furnace baghouse. Of these runs, only the last two were reported, since the first was conducted under abnormal operating conditions. During this first run, effluent gases from the sinter-associated ventilation system were vented to the baghouse. Test 5 was a series of three runs performed on each of the three ducts leading to the blast furnace baghouse. The first run was conducted simultaneously with a run on the uncontrolled emissions, and therefore was not reported for the same reason. The reported test data are a combination of the three baghouse stacks. The data from tests 4 and 5 were conducted using standard methods, and complete process data were provided. An A rating was therefore assigned.

Particle sizing data were conducted concurrently with each of the above test sequences on the blast furnace baghouse stacks (test 5). The tests were conducted on only one of the stacks and therefore does not reflect operating differences among the three different baghouse compartments. Complete process data were provided. As on the total emission rate tests, the first test was conducted under abnormal operating conditions. This test sequence was given an A test rating.

ASARCO: Glover (1976)

A total of eight particulate sampling tests were conducted during the 1976 testing at the blast furnace of ASARCO's lead smelter in Glover, Missouri (Ref. 54). Controlled particulate mass emission rate data and particle sizing data were collected at the blast furnace baghouse. None of the data were considered representative of normal operating conditions and were therefore not reported.

Five Andersen cascade impactor particle sizing tests were performed on one of three stacks from the blast furnace baghouse. Insufficient process data were provided to determine size-specific emission factors directly. Adequate documentation of test procedures was included, but not all five impactor tests were considered of highest reliability. In the experimental setup, a cyclone precutter was used ahead of the impactor. Between 16 and 59 percent of the total catch was captured by this precutter. Three of the test runs (2, 3, and 4) showed nearly identical size distributions with an average precutter capture of 19 percent. Of the other two, the first had the very high precutter capture (59 percent) and the last had a particle mass concentration of 0.010 gr/dscf as compared to an average of 0.006 ±0.001 gr/dscf for the other three tests combined.

Although the data were of very high quality, there were a few restrictions on its representativeness. First, the data were obtained without any process rate data, and therefore could not be directly normalized to produce size-specific emission factors. A second restriction to the data was that the sizing tests were conducted under slightly contrived circumstances. To avoid fluctuations due to irregular emissions during a baghouse cleaning cycle, the sample probes were periodically removed from the stack. This was done because the emission rates are high during a baghouse shake, but the size-specific collection efficiency of a baghouse changes during the period from one shake to the next. Consequently, the data received were not representative of normal operations and are not reported here.

Total emission rate tests using EPA Method 5 were conducted in conjunction with the above tests. Due to a lack of documentation on whether these data represent similar testing conditions to the above particle sizing tests as well as incomplete process data these data were not included in the present study.

ASARCO: Glover (1976) (Tests 6 Through 8)

A total of 26 fugitive particulate emission tests of interest to this study were conducted during the 1976 testing at the ASARCO lead smelter and refinery (Ref. 54). Additional tests were conducted that were not included since they were either not sufficiently well documented, or they were considered unreliable. The tests covered seven different emission points, and were used to develop total particulate emission rates from three process locations around the plant. Of these, four tests were performed using high-volume, five-stage Sierra cascade impactors providing particulate size distribution data. Insufficient testing at all of the emission points required that size-specific emission factors be calculated by combining particulate size distributions and average mass emission factors for each process location tested.

No process rate data were presented for the test period. Production rate data were estimated for both the sinter machine and the blast furnace from previous testing at the same plant. Production rate data were estimated for the ore storage facility from the overall plant production rate limiting process (sinter machine).

Fugitive emission rates from any specific process were estimated by sampling at one or more points in or around the facility. The number of emission points sampled at each facility are listed below with particle sizing test numbers in parentheses:

- A single point at the ore storage area (test 6)
- Three locations within the sinter machine building (test 7)
- Three points including charging (test 8a) and tapping operations (test 8b) at the blast furnace

The particulate size distribution data were collected using standard methods and were given an A-test rating. The resulting size-specific emission rates, as well as the total particulate emission rates, were not reported in adequate detail to determine emission factors with sufficient confidence, and therefore a B-test rating was assigned.

ASARCO: East Helena (1976) (Tests 9 Through 12)

A total of 44 fugitive particulate emissions tests were conducted during the 1976 testing at the ASARCO lead smelter in East Helena, Montana (Ref. 54). Tests conducted at 11 emission points were used to develop total particulate emission rates from four different process locations. Of these, eight tests were conducted using high-volume, five-stage Sierra cascade impactors providing particulate size distribution data.

No process rate data were presented, and therefore no direct calculation of emission factors is possible. Process rate data were estimated from previous testing at the Glover, Missouri lead smelter and refinery operated by ASARCO, using production rates prorated on the basis of annual plant capacity.

Fugitive emission rates from any specific process were estimated by testing one or more emission points in or around that facility. The number of emission points sampled at each facility tested are listed below with particle sizing test numbers shown in parentheses:

- Seven emission points within the sinter machine building (tests 9a and b)
- Three emission points around the blast furnace (tests 10a and b)
- A single emission point at the dross kettle (tests 11a and b)

- A single emission point near the reverberatory furnace (tests 12a and b)

The particulate size distribution data were collected using standard methods and were given an A rating. The resulting size-specific emission rates as well as the total particulate emission rates were reported in inadequate detail to determine emission factors with sufficient confidence, and therefore a B rating was assigned.

4.2.2 Data Analysis

Emission factors for total and size-specific particulate emissions have been developed for the primary lead processing industry. The data are generally good, but not necessarily representative of the industry as a whole, with only two out of five facilities tested.

Size distributions and size-specific emission factors have been developed for controlled blast furnace emissions as well as several fugitive sources. The fugitive emission sources tested were: (1) ore storage area, (2) sinter machine, (3) blast furnace, (4) dross kettle, and (5) reverberating furnace. Tables 34 through 39 and Figures 30 through 35 present the emission factors obtained.

The controlled blast furnace emission factors were obtained from duplicate tests at a single facility. Complete data were provided to determine size-specific emission factors for each test. The overall process size-specific emission factors were calculated from A-rated data using Method 1 (as described in Section 1), but were rated C due to the lack of representative industry-wide data.

The fugitive emission factors were obtained from multiple tests at either one or both of the two facilities tested. Incomplete data were provided to determine size-specific emission factors for each test. The overall process size-specific emission factors were calculated from A-rated size distribution data using Method 2, and were rated D due to the lack of sufficient data as well as the questionable representativeness of the data.

Total particulate emission factors for controlled and uncontrolled emission sources within a primary lead smelter were determined. The point source emission factors do not include data previously compiled in the AP-42 section and therefore the mass emission factors will not be replaced. The fugitive emission factors represent new data and should replace the previous AP-42 emission factors, which were determined from a facility that is no longer operating. The point and fugitive source mass emission factors are presented in Table 40.

TABLE 34. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR BAGHOUSE CONTROLLED EMISSIONS FROM BLAST FURNACE FLUE GASES[a]

EMISSION FACTOR RATING: C

Particle size[b] (μm)	Cumulative mass percent less than stated size	Cumulative emission factors	
		kg/Mg	lb/ton
	Controlled	Controlled	Controlled
15	98	1.17	2.34
10	86.3	1.03	2.06
6	71.8	0.86	1.72
2.5	56.7	0.68	1.36
1.25	54.1	0.65	1.29
1.00	53.6	0.64	1.28
0.625	52.9	0.63	1.27
Total	100	1.20	2.39

[a] Reference 53.

[b] Expressed as aerodynamic equivalent diameter.

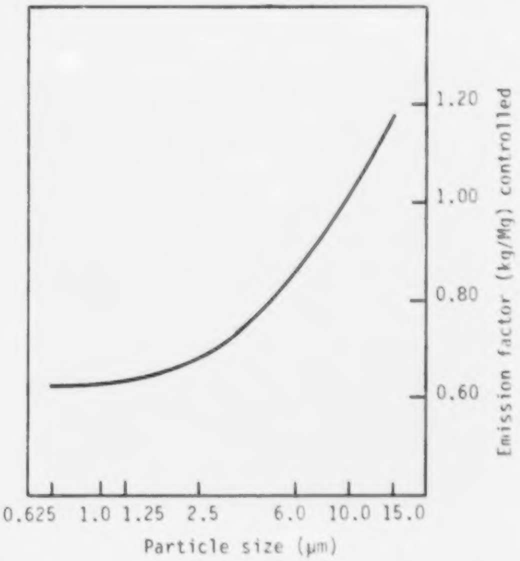

Figure 30. Cumulative size-specific emission factors for baghouse controlled emissions from a blast furnace.

TABLE 35. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR UNCONTROLLED ORE STORAGE FUGITIVE EMISSIONS[a]

EMISSION FACTOR RATING: D

Particle size[b] (µm)	Cumulative mass percent less than stated size	Cumulative emission factors	
		kg/Mg	lb/ton
	Uncontrolled	Uncontrolled	Uncontrolled
15	91	0.011	0.023
10	86	0.010	0.021
6	80.5	0.010	0.020
2.5	69.0	0.009	0.017
1.25	61.0	0.008	0.015
1.00	59.0	0.007	0.015
0.625	54.5	0.007	0.013
Total	100	0.012	0.025

[a] Reference 54.

[b] Expressed as aerodynamic equivalent diameter.

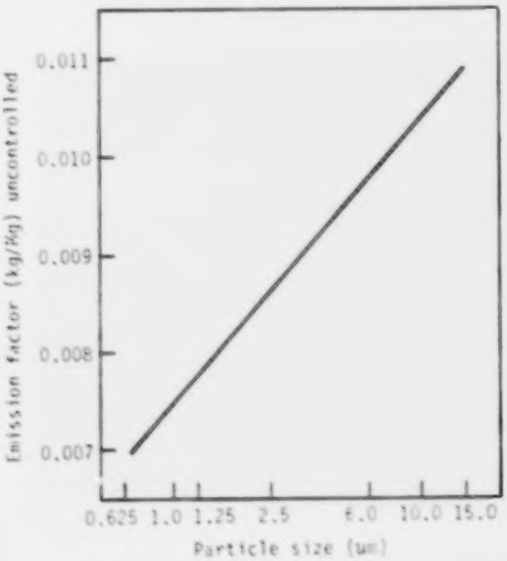

Figure 31. Cumulative size-specific emission factors for uncontrolled ore storage fugitive emissions.

TABLE 36. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR UNCONTROLLED SINTER MACHINE FUGITIVE EMISSIONS[a]

EMISSION FACTOR RATING: D

Particle size[b] (μm)	Cumulative mass percent less than stated size	Cumulative emission factors	
		kg/Mg	lb/ton
	Uncontrolled	Uncontrolled	Uncontrolled
15	99	0.10	0.19
10	98	0.10	0.19
6	94.1	0.09	0.17
2.5	87.3	0.08	0.16
1.25	81.1	0.07	0.15
1.00	78.4	0.07	0.15
0.625	73.2	0.07	0.14
Total	100.0	0.10	0.19

[a] Reference 54.

[b] Expressed as aerodynamic equivalent diameter.

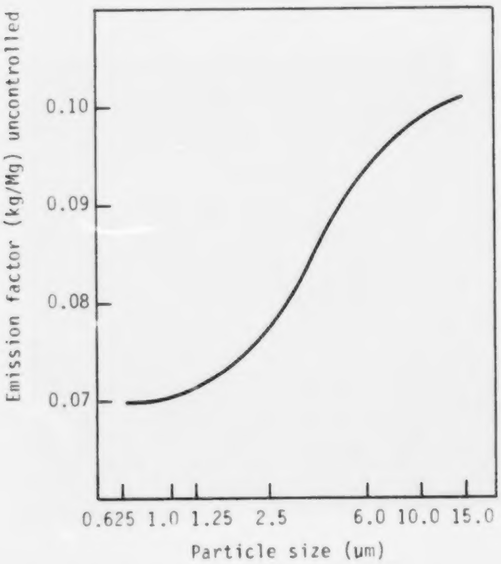

Figure 32. Cumulative size-specific emission factors for uncontrolled sinter machine fugitive emissions.

TABLE 37. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR UNCONTROLLED BLAST FURNACE FUGITIVE EMISSIONS[a]

EMISSION FACTOR RATING: D

Particle size[b] (μm)	Cumulative mass percent less than stated size	Cumulative emission factors	
		kg/Mg	lb/ton
	Uncontrolled	Uncontrolled	Uncontrolled
15	94	0.11	0.23
10	89	0.11	0.21
6	83.5	0.10	0.20
2.5	73.8	0.09	0.17
1.25	65.0	0.08	0.15
1.00	61.8	0.07	0.15
0.625	54.4	0.06	0.13
Total	100.0	0.12	0.24

[a] Reference 54.

[b] Expressed as aerodynamic equivalent diameter.

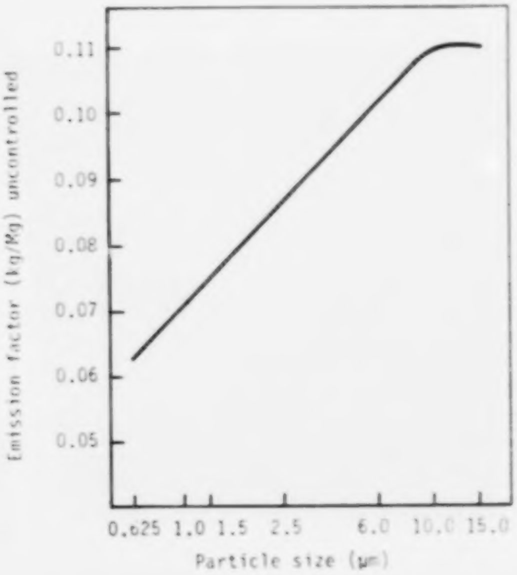

Figure 33. Cumulative size-specific emission factors for uncontrolled blast furnace fugitive emissions.

TABLE 38. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR UNCONTROLLED DROSS KETTLE FUGITIVE EMISSIONS[a]

EMISSION FACTOR RATING: D

Particle size[b] (µm)	Cumulative mass percent less than stated size	Cumulative emission factors kg/Mg	Cumulative emission factors lb/ton
	Uncontrolled	Uncontrolled	Uncontrolled
15	99	0.18	0.36
10	98	0.18	0.35
6	92.5	0.17	0.33
2.5	83.3	0.15	0.30
1.25	71.3	0.13	0.26
1.00	66.0	0.12	0.24
0.625	51.0	0.09	0.18
Total	100.0	0.18	0.36

[a] Reference 54.

[b] Expressed as aerodynamic equivalent diameter.

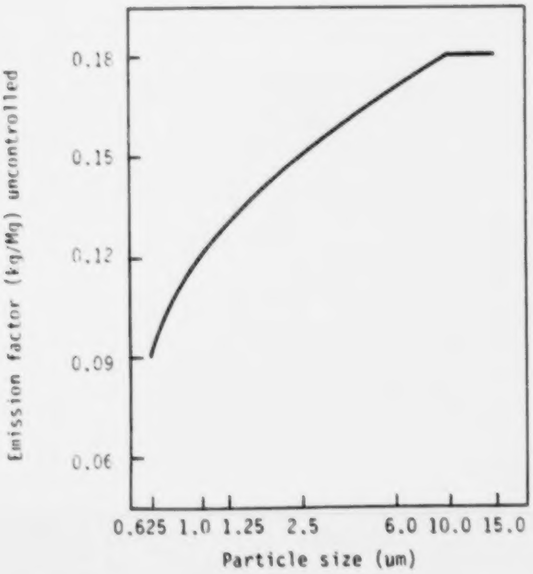

Figure 34. Cumulative size-specific emission factors for uncontrolled dross kettle fugitive emissions.

TABLE 39. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR UNCONTROLLED REVERBERATING FURNACE FUGITIVE EMISSIONS[a]

EMISSION FACTOR RATING: D

Particle size[b] (µm)	Cumulative mass percent less than stated size	Cumulative emission factors kg/Mg	Cumulative emission factors lb/ton
	Uncontrolled	Uncontrolled	Uncontrolled
15	99	0.24	0.49
10	98	0.24	0.48
6	92.3	0.22	0.45
2.5	80.8	0.20	0.39
1.25	67.5	0.16	0.33
1.00	61.8	0.15	0.30
0.625	49.3	0.12	0.24
Total	100.0	0.24	0.49

[a] Reference 54.
[b] Expressed as aerodynamic equivalent diameter.

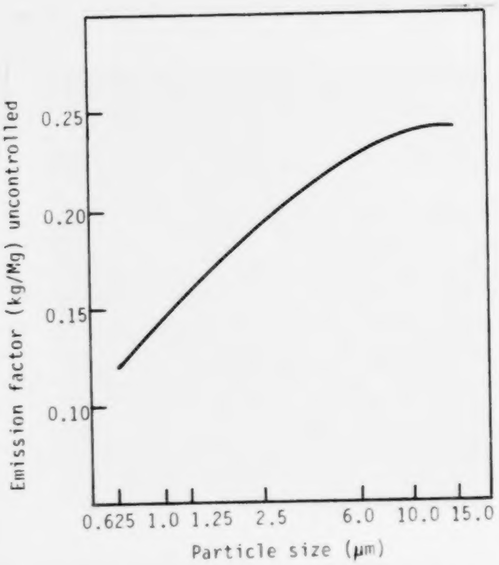

Figure 35. Cumulative size-specific emission factors for uncontrolled reverberating furnace fugitive emissions.

TABLE 40. EMISSION FACTOR TABLE -- PRIMARY LEAD PROCESSING[a]

Process/source	Uncontrolled emissions (kg/Mg)	Uncontrolled emissions (lb/ton)	Emission factor rating	Controlled emissions (kg/Mg)	Controlled emissions (lb/ton)	Emission factor rating
Point source emissions						
Sinter machine	62.3	124.5	C	0.10	0.20	E
Blast furnace	81.8	163.5	C	1.20	2.39	C
Fugitive emissions						
Ore storage	0.012	0.025	D	NA	NA	NA
Sinter machine	0.10	0.19	D	NA	NA	NA
Blast furnace	0.12	0.24	D	NA	NA	NA
Dross kettle	0.18	0.36	D	NA	NA	NA
Reverberatory furnace	0.24	0.49	D	NA	NA	NA

[a] All emission factors based on quantity of lead produced.

4.3 CHEMICAL CHARACTERIZATION

The chemical composition of particulate emissions from primary lead smelters is influenced chiefly by the source ore. Table 44 shows typical analyses of Southeastern Missouri and Western lead ores. Lead and S are the primary constituents of both ores. High-grade Southeastern Missouri ores contain around 75 percent lead, whereas Western ores contain between 45 and 60 percent lead. Zn accounts for up to 15 percent of Western ores and is sometimes recovered in conjunction with lead.

Chemical characterization data of point source particulate emissions have generally been restricted to lead content. Lead content of emissions from the sinter machine and blast furnace range from 6 to 28 percent. Average lead content from a variety of process locations is presented in Table 42.

Chemical characterization data of fugitive emissions are more complete, with X-ray diffraction analysis examining samples for: Pb, PbS, lead sulfate ($PbSO_4$), zinc oxide (ZnO), zinc sulfide (ZnS), calcium carbonate ($CaCO_3$), arsenic trioxide (As_2O_3), calcium sulfate ($CaSO_4$), cadmium oxide (CaO), and Zn. Table 43 presents major species weight percent for several process locations at two primary lead smelters.

TABLE 41. TYPICAL LEAD ORE CONCENTRATE CHEMICAL ANALYSES (PERCENT BY WEIGHT)

Chemical	Southeastern Missouri[a]	Western[b]
Pb	75.5	45 to 60
S	15.2	10 to 30
Fe	1.56	1.0 to 8.0
Zn	1.17	0 to 15
CaO	1.14	tr to 3.0
MgO	0.83	NA
Cu	0.75	0 to 3
Ni	0.15	NA
Co	0.07	NA
As	0.007	0.01 to 0.40
Sb	NA	0.01 to 2.0
Bi	NA	tr to 0.1
Ag	NA	0. to 0.0014
Au	NA	0. to 0.00005
Insolubles	1.2	0.5 to 4.0

[a] Reference 53 mean of two reported analyses.
[b] Reference 54.

TABLE 42. POINT SOURCE PARTICULATE EMISSIONS LEAD CONTENT[a]

Process location	Number of samples	Lead content (percent by weight)
Sinter machine and associated ventilation gases (uncontrolled)	6	10.2
Sinter machine and associated ventilation gases baghouse (controlled)	3	12.6
Blast furnace (uncontrolled)	3	12.8
Blast furnace baghouse (controlled)	3	22.5

[a] Reference 49.

TABLE 43. FUGITIVE EMISSIONS: MAJOR SPECIES BY X-RAY DIFFRACTION[a]

			Chemical species (percent)				
Plant	Process location	Number of samples	Pb	Pbs	$PbSO_4$	ZnO	ZnS
Glover	Ore storage	2	--	75	20	--	5
	Sinter machine	6	--	73	12	--	14
	Blast furnace	3	--	73	10	--	13
East Helena	Ore storage	2	--	50	15	13	23
	Sinter machine	5	8	43	21	--	24
	Blast furnace	2	13	13	8	60	8
	Dross kettles	1	45	40	10	--	5
	Reverberatory furnace	1	30	50	10	5	5

[a] Reference 51.

SECTION 5

SECONDARY LEAD PROCESSING

5.1 OVERVIEW*

The following section is a source category report for particulate matter emissions from the secondary lead processing industry. This section includes a description of the secondary lead industry and the various processes involved in secondary lead production. Sources of particulate matter emissions from the secondary lead production processes are discussed, as is the type of particulate matter emission control equipment used by the industry, for each process. Information concerning particulate matter emission rates and associated particle size distributions for the secondary lead production processes is summarized and reviewed. Size-specific emission factors are then developed from this data and rated according to the criteria outlined in Section 1. Finally, a revised AP-42 section on the secondary lead industry is included.

Secondary lead production is unique among nonferrous metals in that it relies heavily on one source of raw materials, specifically, used lead-acid batteries. More than 60 percent of all secondary lead is traditionally derived from remelting battery-lead plates. Other sources include pipe, cable covering, type metal, solder, drosses, and other byproducts. Returned slag from smelting is also reused (Ref. 47,56).

Secondary lead is smelted down from so-called old and new scrap leads. Old scrap lead consists of discarded, dismantled, or wornout metallic items. New scrap lead or "prompt industrial scrap" is generated at various points of the production process. This production scrap, which has not been used in an end product, is supplied directly to smelters in larger, more uniform lots than old scrap (Ref. 57). Consumption of these various kinds of scrap lead is shown in Table 44.

From a 1981 base, demand for lead is expected to increase at an annual rate of about 1.8 percent through 2000. The growth in lead use is contingent on the development of cost-competitive and reliable electric vehicles for general and new industrial use, major power supply load-leveling applications, and continuing high growth for uninterrupted power supply systems. Moderating effects on this projected growth are the current EPA

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*Much of the industry description is taken from Reference 55.

TABLE 44. ANNUAL CONSUMPTION OF SCRAP LEAD IN THE UNITED STATES

Scrap lead type	1975[a] (tons)	1975[a] (Mg)	1982[b] (tons)	1982[b] (Mg)
New scrap[c]				
Dross and residues	136,066	123,416	73,803	66,953
Old scrap[d]				
Soft lead	32,642	29,607	31,603	28,670
Hard lead	26,912	24,410	21,705	19,690
Cable lead	50,569	45,868	4,130	3,747
Battery plates	623,448	565,486	732,121	664,169
Mixed babbitt	3,515	3,188	4,305	3,905
Solder and tinny lead	11,250	10,204	18,481	16,766
Type metals	19,820	17,977	7,503	6,807
Old scrap total	768,156	696,740	819,848	743,744
Total	904,222	820,156	893,651	810,697

[a] Reference 59.
[b] Reference 58.
[c] Lead scrap, generated during the fabrication of lead products.
[d] Lead scrap derived from wornout, damaged, or obsolete fabricated products.

regulations which reduce the use of lead additives in gasoline as octane improves together with a general concern over lead in the environment. The use changes represent some variations in the end-use pattern, which will be reflected in considerably less dissipation of the metal into the general environment and greater recycling by the secondary lead industry. By the year 2000, secondary lead is expected to supply about 60 percent of the total U.S. demand, as opposed to a little over 50 percent in 1983.

In 1983, the secondary lead industry was comprised of about 40 major operating plants, which produced over 95 percent of the recycled metal. Lead was consumed by approximately 450 firms.

A very wide variation normally occurs in annual production for individual smelters. Viewed over a period of months, production of secondary lead is an intermittent operation. It is unusual for a smelter to operate continuously up to capacity. Plants may be shut down for a period of time and started up again when market conditions are more favorable. Therefore, annual production of a plant is not directly determined by daily capacity. Secondary lead refinery capability utilization during 1983 was only 43 percent due to a pervasive shortage of scrap at acceptable prices.

Despite its concentration in the hands of a few predominant companies which produce most of the total output, the secondary lead industry is fairly well dispersed geographically. Secondary lead smelters are present in all 10 EPA regions. The areas of highest concentration of secondary lead smelters are Chicago, Illinois; the Baltimore-Washington industrial corridor; and Perth Amboy, New Jersey. These areas provide most of the old and new scrap utilized by secondary lead smelters in the form of discarded batteries, zinc, and copper alloys.

5.1.1 Secondary Lead

Smelting and Refining Process

The production of refined lead products from recycled scrap is typical of the secondary smelting industry. The scrap is pretreated in preparation for smelting, after which the final stages of refining and casting result in the final product. Secondary lead products include bullion of varying degrees of hardness, alloys, and oxides. The oxides are battery oxides (Pb and PbO) and pigments (Pb_3O_4). Figure 36 is a schematic of the representative process involved in secondary lead production.

Pretreatment includes a variety of operations that result in a fairly uniform material for subsequent smelting operations. The primary source material used is batteries and requires separating lead plates from casing materials. Drosses, casing residues, and oversized scrap must be crushed to a size suitable for smelting. Source material such as lead-sheathed cable and wire, aircraft tooling die scraps, as well as residues and drosses, can be pretreatd by sweating. In either the rotary/tube or reverberatory sweating processes, the source material is heated such that the lead content melts and can therefore be mechanically removed from the waste scrap.

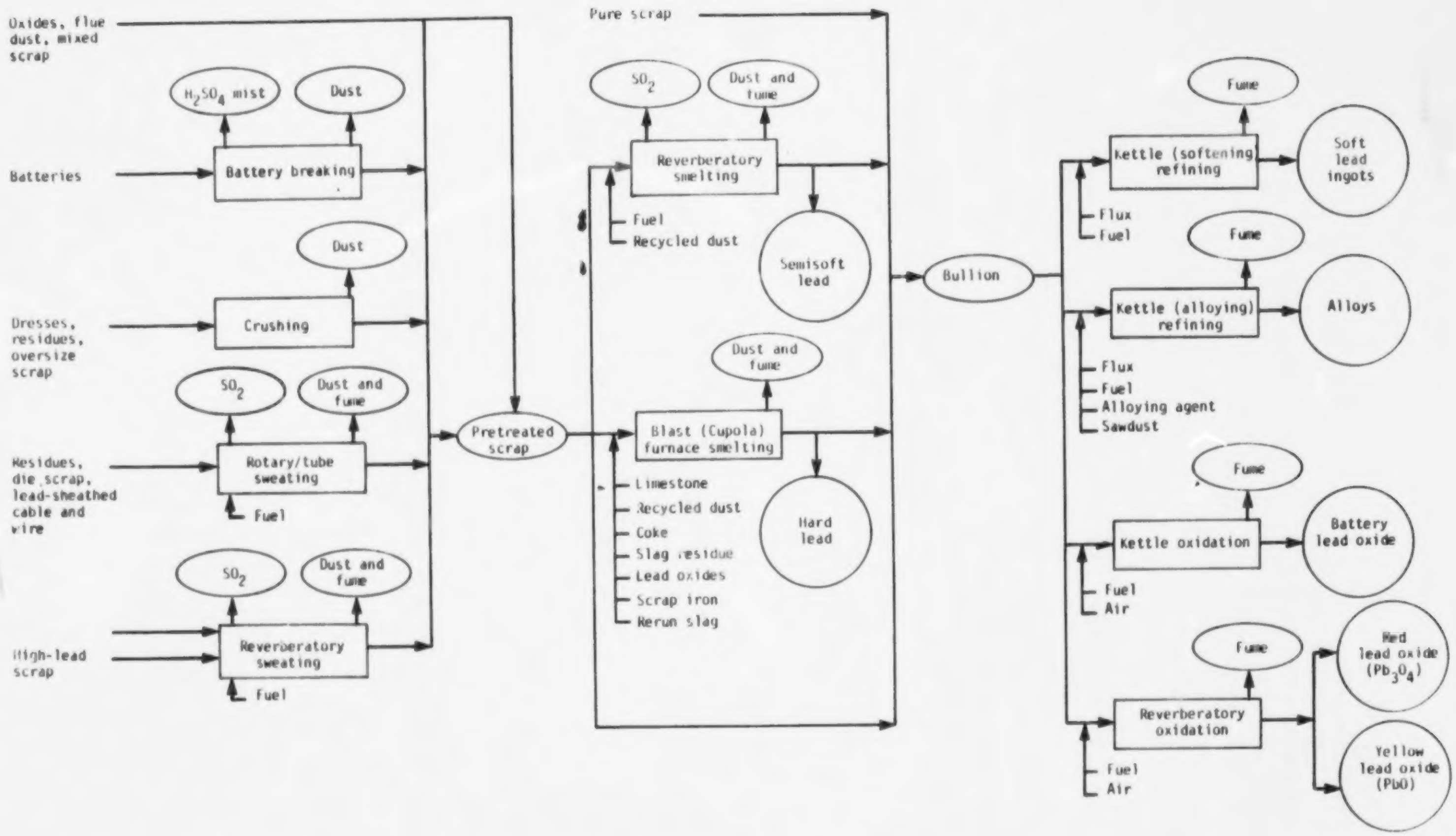
Oxides, flue dust, mixed scrap
Batteries
Dresses, residues, oversize scrap
Residues, die scrap, lead-sheathed cable and wire
High-lead scrap
H_2SO_4 mist
Dust
Battery breaking
Dust
Crushing
SO_2
Dust and fume
Rotary/tube sweating
Fuel
SO_2
Dust and fume
Reverberatory sweating
Fuel
Pretreated scrap
Pure scrap
SO_2
Dust and fume
Reverberatory smelting
Fuel
Recycled dust
Semisoft lead
Dust and fume
Blast (Cupola) furnace smelting
Limestone
Recycled dust
Coke
Slag residue
Lead oxides
Scrap iron
Rerun slag
Hard lead
Bullion
Fume
Kettle (softening) refining
Flux
Fuel
Soft lead ingots
Fume
Kettle (alloying) refining
Flux
Fuel
Alloying agent
Sawdust
Alloys
Fume
Kettle oxidation
Fuel
Air
Battery lead oxide
Fume
Reverberatory oxidation
Fuel
Air
Red lead oxide (Pb_3O_4)
Yellow lead oxide (PbO)

Figure 36. Process schematic secondary lead smelting and refining.

Two-thirds of the output of the secondary lead industry is processed in blast furnaces or cupolas. The remainder of smelting is done in either reverberatory or port furnaces (Ref. 60).

Reverberatory furnaces produce what is termed semisoft lead, containing typically from 3 to 4 percent Sb and less than 0.05 percent Cu (Ref. 56). When a smelter is operating, reverberatory furnaces may operate on a continuous basis and are used in sweating operations and in reclaiming lead from oxides and drosses. Sweating utilizes differences in melting point temperatures to separate lead from other metals. Material for sweating and for reclamation from lead oxides and drosses may be charged in the reverberatory furnace at the same time. Such a furnace radiates heat from burners and the refractory lining into the metal charge within it. The furnace operates at a temperature of about 2,300°F (1,260°C) and at near atmospheric pressure so that air will not leak in. Air blown through the molten metal eliminates impurities. Attempts are made to keep as much heat as possible in the furnace. Only enough draft is provided to remove smoke and fumes. Dross formed in the furnace floats on top of the molten metal and is removed periodically in an operation known as slagging. The slag may be rerun later in a blast furnace. The lead product is periodically tapped into molds. Figure 37 shows a process schematic for a lead reverberatory furnace.

External hoods are used with the objective of passing all smoke and fumes to a collector. To keep cool air out of the furnace, ventilating air for all the hoods is similarly vented. The spout through which the molten lead product pours is the only exception to the hooding. The collected dust is valuable for recycling as fines, either in a reverberatory or a blast furnace. In a continuous operation, a typical weight balance of material shows:

- Forty-seven percent metal recovery as lead product
- Forty-six percent recovery of slag, which may be at least partially recharged
- Seven percent loss as smoke and fumes

Blast furnaces produce what is termed hard or antimonial lead containing as much as 10 percent Sb as well as small amounts of As, Cu, Ni, and Sn from source materials comprised of pretreated scrap, antimonial slag, and blast furnace rerun slag. Cast-iron scrap, limestone, and coke are added as fluxing and reducing agents. A blast furnace is batch-fed from a hopper or feed car near the top at a fairly constant rate, while molten lead is continuously tapped from the bottom. Slag is intermittently tapped as required. Combustion air is introduced to the blast furnace through tuyeres located along the bottom of the furnace. Figure 38 shows a typical blast furnace process schematic including associated cooling and particulate control equipment.

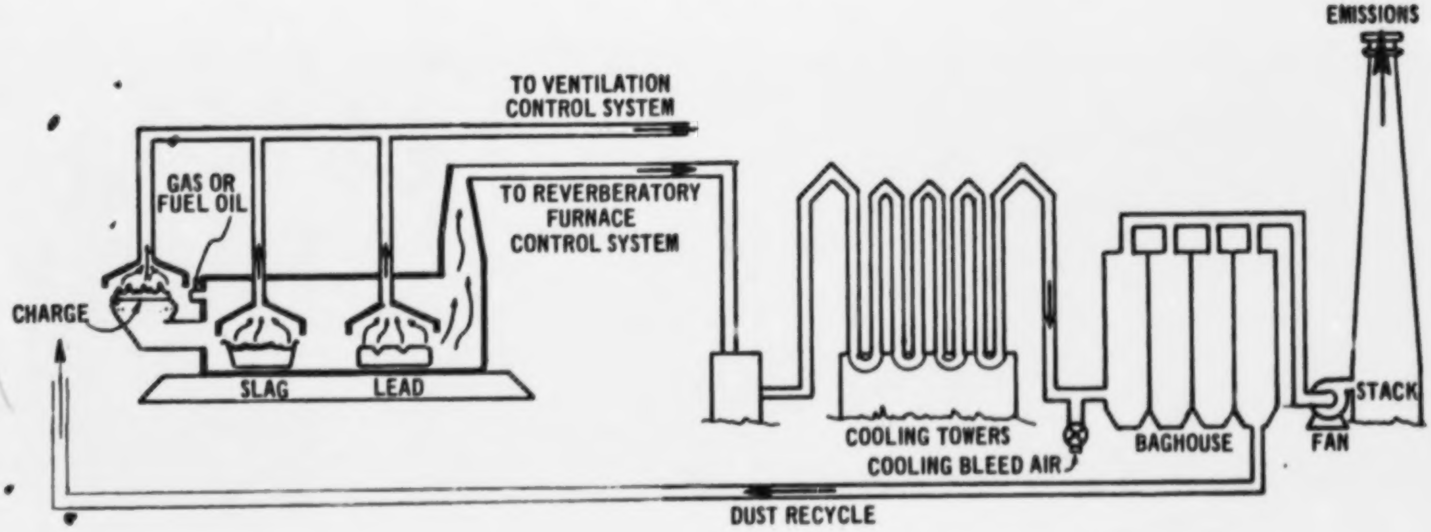
EMISSIONS
TO VENTILATION CONTROL SYSTEM
GAS OR FUEL OIL
TO REVERBERATORY FURNACE CONTROL SYSTEM
CHARGE
SLAG
LEAD
STACK
COOLING TOWERS
COOLING BLEED AIR
BAGHOUSE
FAN
DUST RECYCLE

Figure 37. Lead reverberatory furnace (Ref. 51).

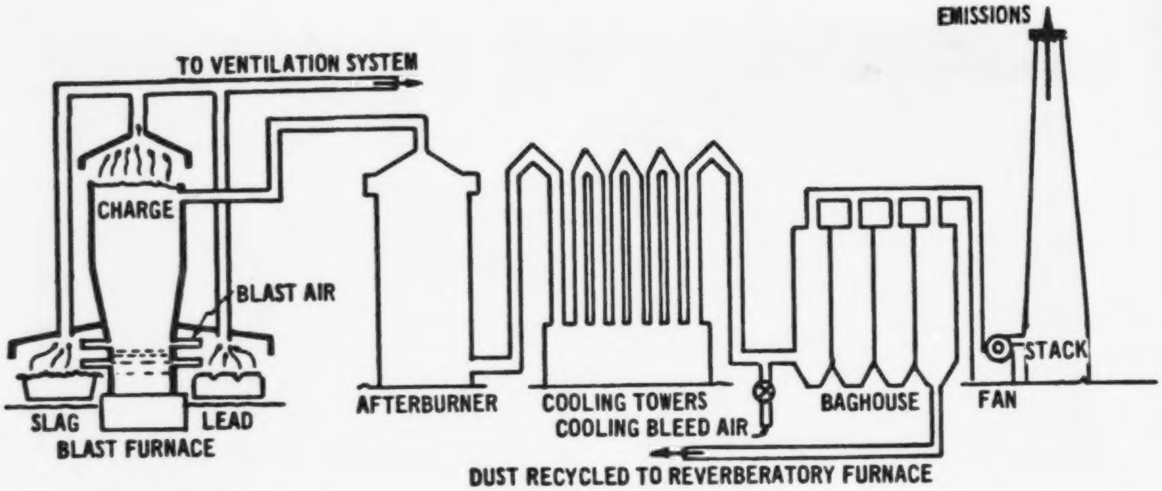
EMISSIONS
TO VENTILATION SYSTEM
CHARGE
BLAST AIR
SLAG
LEAD
BLAST FURNACE
AFTERBURNER
COOLING TOWERS
COOLING BLEED AIR
BAGHOUSE
FAN
STACK
DUST RECYCLED TO REVERBERATORY FURNACE

Figure 38. Secondary processing lead blast furnace (Ref. 51).

A typical blast furnace may be rated at 50 ton/day (45 Mg/day) of product with a flowrate of about 15,000 dry standard cubic feet (dscfm) (425 nm^3/min). New furnaces range in size from 20 to 80 ton/day (18 to 73 Mg/day) ingot production with a gas flowrate of 10,000 to 40,000 dscfm (283 to 1,133 nm^3/min) (Ref. 51). Often blast and reverberatory furnaces in a single installation combine the effluents that are run into a brick-lined chamber with an afterburner. The afterburner is necessary to incinerate oily and sticky material and to convert CO to CO_2. No afterburner is required with the reverberatory furnace, previously mentioned, since the excess air necessary for combustion together with the operating temperature ensure that CO and hydrocarbon materials are fully incinerated.

Pot furnaces use a batch process to remelt lead for alloying or refining. At a temperature range between 600° and 900°F (320° and 380°C), the process may take from a few hours to more than 2 days. The metal is fed into open top kettles that are ceramic-lined and usually fired by natural gas burners placed underneath. The open top of the pot is hooded so that lead oxide fumes will not escape into the working area. A soft lead of high purity (which may exceed 99.0 percent lead) can be produced by the removal of Cu and Sb. A hard lead product results from removing As, Cu, and Ni. For alloying, ingots of a specified metal are added in the desired percentages. Cu, Sn, As, Sb, and Ni are commonly employed in alloys. Since the pot furnace is not direct-fired and the charge is not subject to the same degree of turbulence as in blast and reverberatory furnaces, the quantity of particulate matter emitted is much less than from these furnaces.

5.1.2 Particulate Emission Sources

Particulate emissions are generated as part of the normal operation at a secondary lead processing plant. Dust and/or metallic fumes are generated by nearly every major operation within a plant. Most point sources of emissions are ducted to appropriate control equipment, either directly in the case of flue emissions or indirectly through the use of ventilation hoods for such sources as charging and tapping ports in a blast furnace. Fugitive emissions, however, do occur for sources that cannot be practically controlled through the use of ventilation hoods, or where the ventilation hoods cannot completely enclose the source from the surrounding environment.

Ventilation hoods and particulate control systems employing baghouses minimize fugitive emissions from a variety of sources within a typical secondary lead processing plant. These sources include: (1) battery breaking, (2) dross, residue, and scrap crushing, (3) sweating furnaces, (4) blast furnace charging and tapping port, (5) reverberatory furnace charging ports, furnace exhaust, slag and metallic lead repositories, and (6) holding, refining, and oxidizing kettles. Large quantities of dust and fume are also emitted from the exhaust stack of a blast furnace.

Blast and reverberatory smelting furnaces account for the majority of secondary lead processing particulate emissions. These emissions contain oxides and sulfides of lead, small amounts of other elements, coke fuel, and oil vapor. The high temperature used in a reverberatory furnace (approximately 1,260°C (2,300°F)) accounts for a relatively high-mean loading (in pounds per ton of charge) of oxides of sulfur, chiefly SO_2. The H_2SO_4 in smelted lead batteries accounts for much of the sulfur emissions from a typical furnace, along with casings and other impurities charged.

The particulate emission rates from secondary lead smelters are influenced by a variety of operational parameters. These factors (Ref. 56) have been identified as:

- Production rate
- Quality of charge (i.e., increase in dirt or oil on the scrap increases emissions)
- Method of charge (i.e., adding essentially all of the charge at the beginning of the heating process results in lower emissions than by intermittently charging a hot operating furnace)
- Fuel rate
- Oxygen rate
- Slag cover (i.e., although a slag layer reduces loss of lead due to oxidation, a thick layer tends to harden, increasing lead oxide emissions; prior to the time of hardening, mass emissions are decreased with increasing slag layer thickness)
- Length of time over which a charge is smelted
- Slag fines charged to the furnace (i.e., an increase in these results in a higher rate of particulate emissions)
- For blast furnace, rate of air blowing through the tuyeres

5.1.3 Particulate Emissions Controls

In the past, various control methods have been used in secondary lead smelters to meet state and local requirements for particulate removal and to recover the lead dust valuable for recycling. These have included centrifugal dust collectors, settling chambers, and low-energy scrubbers. In the Background Information Document for the Proposed New Source Performance Standard, it was noted that: "At well-controlled secondary lead smelters, either baghouses or high-energy scrubbers are used to collect dust and fumes from the furnace." It predicted further: "The predominant control devices for the secondary lead industry are expected to be fabric filters, along with a small number of high-energy scrubbers" (Ref. 51). Apparently, all plants may now have baghouses.

Baghouses used to control emissions from secondary lead smelters commonly employ a pull-through, tubular bag made of either Dacron or fiberglass. To facilitate maintenance, the baghouses are usually compartmentalized. Because the temperature of the gas is very high when it leaves the furnace stack (up to 1,350°F (730°C)), it is necessary to employ cooling measures that reduce the temperature to about 500°F (260°C) for fiberglass fabric filters and to about 300°F (149°C) for Dacron filters. The temperature is reduced by passing the gas through radiation or water-jacketd cooling ducts. The cooling duct system may use a water spray and/or U-tube coolers. Although dilution air may also be introduced to effect cooling, the volume of gas that may be pulled is limited by the capacity of the system fan, so that the success of the system depends on radiation and/or water-cooling. It is also necessary to ensure that sparks and other burning materials do not come in contact with the fabric of the filter bag. As previously noted, an afterburner is employed with blast furnaces to ensure complete combustion of such material before it enters the baghouse. To prevent condensation within the baghouse, the entering gas temperature must be maintained at 50°F (28°C) above the dewpoint; otherwise condensation results in caking on the bags and a pressure buildup that will ultimately rupture the fabric. Also, sulfur in the cake forms damaging acids.

Venturi scrubbers have also been used for emission control, although less widely than baghouses. These scrubbers commonly employ a pressure drop between 30 and 100 in. H_2O (7 and 25 kPa), whereas baghouses have pressure drops up to 4 in. H_2O (1 kPa). The efficiency of the scrubber is primarily controlled by the pressure drop and secondarily by the rate of water flow (a water quench is typically used which lowers gas temperature).

5.2 SECONDARY LEAD PROCESSING EMISSION FACTORS

The following subsection outlines the methodology involved in the development of size-specific emission factors for various processes within the secondary lead processing industry. The data from which the emission factors are developed are reviewed, analyzed, and rated according to the guidelines presented in Section 1.

5.2.1 Data Review

Total and size-specific particulate emissions data have been obtained from 24 emission tests at secondary lead smelters. A summary of these tests, showing test site, emission source, control device, the type of data obtained, when the test was conducted, and the quality of the data is presented in Table 45.

Total particulate emissions data were located for blast and reverberatory furnaces, refining kettles, and pigging operations from nine different references. All other emission sources, including data for fugitive emissions reported in previous AP-42 sections were determined to be based on engineering estimates and are thus not included in this report. Table 46 presents the total particulate emissions data obtained. This includes controlled and uncontrolled emissions data where available.

Size-specific particulate emissions data were obtained from one source for blast furnace operations only. The data obtained were for both process

TABLE 45. SUMMARY OF PARTICULATE EMISSIONS TESTS SECONDARY LEAD PROCESSING

Test no.	Source location	Emission point	Control device(s)	Type of data[a]	Test date	Test rating	Reference
1	East Penn Manufacturing	Blast furnace charging hood	--[b]	1,2	August 1980	B,A	61
2	East Penn Manufacturing	Blast furnace metal tapping head	--	1,2	August 1980	B,A	61
3	East Penn Manufacturing	Refining kettle	--	2	August 1980	B	61
4	East Penn Manufacturing	Casting	--	2	August 1980	B	61
5	East Penn Manufacturing	Blast furnace ventilation gases	Baghouse	1,2	August 1980	B,A	61
6	East Penn Manufacturing	Blast furnace slag tapping hood	--	1,2	August 1980	B,A	61
7	East Penn Manufacturing	Blast furnace slag tapping hood	Baghouse	2	August 1980	B	61
8	East Penn Manufacturing	Blast furnace process flue	Baghouse	1,2	August 1980	B,A	61
9	Revere Smelting & Refining	Blast furnace	Venturi	2	December 1971	A	62,51
10	General Battery Corp	Blast furnace	Afterburner, water spray, baghouse, and venturi	2	December 1971	A	51,63
11	NA[c]	Blast furnace	--	2	1972	A	64
12	NA	Blast furnace	Afterburner, cyclone, and baghouse	2	1972	A	51,64

(continued)

[a] 1 = Particle size distribution.
2 = Total particulate.

[b] -- = uncontrolled.

[c] NA -- Not available.

TABLE 45. (Continued)

Test no.	Source location	Emission point	Control device(s)	Type of data[a]	Test date	Test rating	Reference
13	NA[c] Manufacturing	Blast furnace	--[b]	2	1972	A	64,65
14	NA Manufacturing	Blast furnace	Afterburner and baghouse	2	1972	A	51,64 65
15	NA Manufacturing	Blast furnace	Afterburner and baghouse	2	1972	A	51,64
16	N.L. Industries	Blast furnace	--	2	November 1971	A	66
17	N.L. Industries	Blast furnace	Cyclone, afterburner, and baghouse	2	November 1971	A	51,66
18	Quemetco, Inc.	Reverberatory furnace	--	2	January 1972	A	67
19	Quemetco, Inc.	Reverberatory furnace	Gravity settler, cyclone, and baghouse	2	January 1972	B	51,67
20	N.L. Industries	Reverberatory furnace	--	2	February 1972	A	68
21	N.L. Industries	Reverberatory furnace	Wet cyclone and baghouse	2	February 1972	A	51,68
22	NA	Reverberatory furnace	--	2	1972	A	64,65
23	NA	Reverberatory furnace	Baghouse	2	1972	A	51,64 65

[a] 1 = Particle size distribution.
2 = Total particulate emission rates.

[b] -- = uncontrolled.

[c] NA -- Not available.

TABLE 46. PARTICULATE EMISSION RATE TEST DATA

Test no.	Production rate (ton/hr)	Emission rate (lb/hr)	Emission factor[a]		Emission test rating
			(lb/ton)	(kg/Mg)	
Uncontrolled blast furnace emissions[b]					
Process flue:					
11	3.9[c]	224.0	57.4	28.7	A
13	0.8[c]	229.0	286.0	143.0	A
16	3.0[d]	NR[e]	196.0	98.0	A
Ventilation:					
1,2,6	214.0	272.0	127.0	63.5	A
Controlled blast furnace emissions					
8	2.45	1.81	0.74	0.37	A
8	2.56	0.57	0.22	0.11	A
9	1.50	NR	1.90	0.95	A
9	1.15	NR	1.44	0.72	A
9	1.25	NR	2.02	1.01	A
10	4.20	NR	2.71	1.36	A
10	4.88	NR	1.88	0.94	A
10	3.50	NR	4.24	2.12	A
12	3.9[c]	1.34	0.34	0.17	A
14	0.8[c]	3.9	4.88	2.44	A
15	2.2[c]	5.4	2.43	1.21	A
17	2.5	NR	3.70	1.85	A
17	3.0	NR	2.62	1.31	A
Uncontrolled reverberatory furnace emissions					
18	2.10	NR	483.0	241.0	A
20	2.40	NR	313.0[f]	156.0	A
22	0.75[c]	130.0	173.0	87.0	A
Controlled reverberatory furnace emissions					
19	2.10	NR	0.79	0.39	A
19	2.10	NR	0.53	0.26	A
19	2.10	NR	1.16	0.58	A
19	2.10	NR	0.82	0.41	A
21	2.40	NR	0.99	0.49	A
21	2.40	NR	1.06	0.53	A
21	2.40	NR	1.16	0.58	A
23	0.75[c]	1.16	1.55	0.77	A
Uncontrolled refining kettle emissions					
3	2.34	0.095	0.04	0.02	A
3	2.28	0.057	0.03	0.01	A
Uncontrolled casting emissions					
4	2.34	0.117	0.05	0.03	A
4	2.22	0.073	0.03	0.02	A

[a] All emission factors based upon ton of lead product.

[b] Uncontrolled blast furnace emissions total of blast furnace process flue plus ventilation gases associated with charging and tapping hoods.

[c] Estimated at 0.6 x process rate per Reference 51.

[d] Average of three sample production rates during controlled emission rate test no. 17.

[e] NR = not reported (in AP-42 Section emission factor backup file test summaries).

[f] Data reported as 56.4 lb particulate per ton charge with 5.54 ton charge per ton lead produced calculated from other reported data.

flue gases as well as associated ventilation gases coming from charging and tapping hoods. The data include controlled emissions from both sources, but uncontrolled emissions from blast furnace associated ventilation gases only.

East Penn Manufacturing (Tests 1 through 8)

A total of 16 particulate sampling tests at eight sites applicable to the current study were conducted during the August 1980 testing at the East Penn Manufacturing smelter (Ref. 61). Testing at this plant was conducted at the blast furnace, refining kettles, and pigging operations. Size-specific emission factor data from this source are presented in Table 47. Associated data for calculating total emission factors is presented in Table 48.

Particle sizing data were collected using a seven-stage (with backup filter) University of Washington cascade impactor. Size-specific emission rates were determined from this data, but reported at as many as 18 preselected particle size cutpoints using a cubic-spline interpolation of the new data. Size-specific lead content was determined by segregating the collected sample into three or four size groupings, digesting by EPA Method 12, and determining lead content using atomic absorption spectrophotometry (AAS).

Total particulate emissions data were collected using a modified EPA Method 12 impinger train. Stack temperature and velocity, total particulate emissions, and lead content were calculated from the data collected. Lead content was determined by AAS.

Blast furnace emissions were obtained from tests 1, 2, 5, 6, 7, and 8. Total mass emissions and size-specific process emissions were measured only after the control device (test 8), and so no uncontrolled emissions were reported. Uncontrolled total mass emissions and size-specific emissions were obtained for ventilation gases at the blast furnace charging metal tapping and slag tapping hoods (tests 1, 2, and 6). Controlled total mass emissions and size-specific emissions were obtained for blast furnace charging and tapping hoods (tests 5 and 7). Two separate baghouses were used to clean these ventilation gases. One treated the slag tapping hood alone with controlled and uncontrolled total emission factors of 0.03 and 12.55 lb/ton (0.02 and 0.78 kg/Mg), respectively. The other baghouse treated the charging and metal tapping hoods as well as ventilation hoods on the refining kettles and pigging operations. The combined emission factors of the refining and pigging operations, 0.04 lb/ton (0.02 kg/Mg) were considered insignificant compared to the charging and metal tapping operations, 125.5 lb/ton (62.7 kg/Mg) and therefore unlikely to significantly effect the resulting size distribution from this baghouse. Similarly, while the size distribution for the total blast furnace ventilation gases is unlikely to be effected by the small quantity of emissions from the slag tapping baghouse, 0.03 lb/ton (0.02 kg/Mg) as compared to the charging and metal tapping baghouse emissions, 0.90 lb/ton (0.045 kg/Mg). The size-specific emission factors were calculated from a combined total emission factor of 0.93 lb/ton (0.47 kg/Mg).

TABLE 47. SUMMARY OF THE B-RATED DATA[a]

				Particle size distribution														
Plant/type	Emission Source	Run		Total	23.71	17.78	13.34	10.00	7.50	5.62	4.22	3.16	2.37	1.78	1.33	1.00	0.75	0.56
East Penn Manufacturing Lyons	Blast furnace charging hood	1a	d_{50} (m)	98.4	21.7	21.0	20.1	19.4	18.7	17.9	17.2	16.4	12.8	9.9	5.4	2.3	0.9	0.3
			Cum. % <d_{50}	100.0	22.1	21.3	20.5	19.7	19.0	18.2	17.5	16.7	13.0	10.1	5.5	2.3	0.9	0.3
East Penn Manufacturing Lyons	Blast furnace charging hood	1b	d_{50} (m)	150.9	79.7	78.9	78.0	77.1	76.4	75.8	74.5	73.3	67.3	61.4	59.6	38.8	17.7	7.4
			Cum. % <d_{50}	100.0	52.8	52.3	51.7	51.1	50.6	50.2	49.4	48.6	44.6	40.7	39.5	25.7	11.7	4.9
East Penn Manufacturing Lyons	Blast furnace metal hood	Average	d_{50} (m)	124.7	50.7	49.9	49.1	48.2	47.5	46.8	45.9	44.9	40.0	35.7	32.5	20.5	9.3	3.8
			Cum. % <d_{50}	100.0	40.7	40.0	39.4	38.6	38.1	37.5	36.8	36.0	32.1	28.6	26.1	16.4	7.5	3.0
East Penn Manufacturing Lyons	Blast furnace metal tapping hood	2a	d_{50} (m)	0.67	0.67	0.61	0.60	0.60	0.59	0.59	0.58	0.56	0.54	0.49	0.42	0.31	0.16	0.08
			Cum. % <d_{50}	100.0	90.7	90.3	89.7	89.0	88.4	87.7	85.9	83.8	80.2	73.0	62.7	46.5	24.4	11.7
East Penn Manufacturing Lyons	Blast furnace metal tapping hood	2b	d_{50} (m)	0.89	0.78	0.78	0.78	0.77	0.77	0.76	0.74	0.73	0.69	0.62	0.51	0.37	0.22	0.10
			Cum. % <d_{50}	100.0	88.1	87.6	87.1	86.6	86.1	85.5	83.7	81.7	77.8	69.4	56.8	41.2	24.7	11.4
East Penn Manufacturing Lyons	Blast furnace metal tapping hood	Average	d_{50} (m)	0.78	0.70	0.69	0.69	0.68	0.68	0.67	0.66	0.64	0.61	0.55	0.46	0.34	0.19	0.09
			Cum. % <d_{50}	100.0	89.2	88.8	88.2	87.6	87.1	86.4	84.6	82.6	78.8	70.9	59.3	43.5	24.6	11.6
East Penn Manufacturing Lyons	Blast furnace slag tapping hood	6a	d_{50} (m)	1.33	1.28	1.26	1.25	1.23	1.21	1.18	1.15	1.12	1.03	0.93	0.69	0.32	0.13	0.05
			Cum. % <d_{50}	100.0	96.2	95.1	93.9	92.5	90.8	88.8	86.6	84.1	77.7	70.2	52.0	24.4	9.4	3.7
East Penn Manufacturing Lyons	Blast furnace slag tapping hood	6b	d_{50} (m)	1.76	1.22	1.21	1.18	1.16	1.13	1.09	1.03	0.98	0.89	0.80	0.60	0.27	0.11	0.04
			Cum. % <d_{50}	100.0	69.6	68.6	67.3	65.8	64.0	61.7	58.8	55.4	50.7	45.4	34.0	15.3	6.3	2.4
East Penn Manufacturing Lyons	Blast furnace slag tapping hood	Average	d_{50} (m)	1.55	1.25	1.24	1.22	1.19	1.17	1.13	1.09	1.05	0.96	0.87	0.65	0.30	0.12	0.05
			Cum. % <d_{50}	100.0	81.0	80.0	78.7	77.3	75.5	73.4	70.8	67.8	62.3	56.1	41.7	19.2	7.6	3.0
East Penn Manufacturing Lyons	Blast furnace ventilation gases (uncontrolled)	Average	d_{50} (m)	1.27	52.7	51.8	51.0	50.1	49.4	48.6	47.7	46.6	41.6	37.1	33.6	21.1	9.8	3.9
			Cum. % <d_{50}	100.0	41.4	40.8	40.2	39.4	38.8	38.3	37.5	36.7	32.7	29.2	26.5	16.6	7.7	3.1
East Penn Manufacturing Lyons	Blast furnace sanitary baghouse exhaust	5a	d_{50} (m)	1.49	1.39	1.33	1.27	1.21	1.15	1.10	1.04	0.98	0.89	0.78	0.66	0.49	0.29	0.12
			Cum. % <d_{50}	100.0	93.3	89.4	85.2	80.9	76.9	73.6	69.8	65.8	59.7	52.4	44.5	32.8	19.3	8.1
East Penn Manufacturing Lyons	Blast furnace sanitary baghouse exhaust	5b	d_{50} (m)	0.31	0.31	0.31	0.30	0.30	0.29	0.29	0.28	0.27	0.26	0.26	0.19	0.08	0.06	0.05
			Cum. % <d_{50}	100.0	99.2	98.6	97.9	96.7	95.0	92.8	91.6	86.3	84.0	82.7	62.3	25.6	20.1	14.9
East Penn Manufacturing Lyons	Blast furnace ventilation gases (uncontrolled)	Average	d_{50} (m)	0.90	0.85	0.82	0.79	0.75	0.72	0.69	0.66	0.62	0.57	0.52	0.43	0.28	0.17	0.08
			Cum. % <d_{50}	100.0	94.3	91.0	87.4	83.6	80.0	76.9	73.6	69.3	63.9	57.6	47.6	31.6	19.4	9.3
East Penn Manufacturing Lyons	Blast furnace process baghouse	8a	d_{50} (m)	0.74	0.73	0.72	0.68	0.66	0.65	0.62	0.60	0.57	0.53	0.45	0.35	0.24	0.14	0.09
			Cum. % <d_{50}	100.0	99.3	97.3	92.5	89.7	87.2	84.3	80.6	77.0	71.8	61.0	46.8	32.4	19.5	12.7
East Penn Manufacturing Lyons	Blast furnace process baghouse	8b	d_{50} (m)	0.22	0.20	0.20	0.19	0.19	0.18	0.18	0.17	0.16	0.14	0.12	0.10	0.07	0.05	0.05
			Cum. % <d_{50}	100.0	91.5	90.2	88.4	86.2	83.2	79.6	75.4	70.8	65.7	56.6	43.8	29.9	20.4	12.5
East Penn Manufacturing Lyons	Blast furnace process gases (uncontrolled)	Average	d_{50} (m)	0.48	0.47	0.46	0.44	0.43	0.41	0.40	0.38	0.36	0.34	0.29	0.22	0.15	0.10	0.06
			Cum. % <d_{50}	100.0	97.5	95.7	91.6	88.9	86.3	83.2	79.4	75.6	70.4	60.0	46.1	31.8	19.8	12.7

[a] Source: Reference 61

TABLE 48. MASS EMISSION FACTOR DATA FOR SIZE-SPECIFIC EMISSION FACTOR CALCULATIONS[a]

Test number	Daily production (ton)	Production rate[b] (ton/hr)	Emission rate (lb/hr)	Emission factor[c] (kg/Mg)	(lb/ton)
Uncontrolled blast furnace ventilation gases					
Charging hood					
1a	45.2	1.88	185	49.2	98.4
1b	56.1	2.34	353	75.5	150.9
Metal tapping hood					
2a	45.2	1.88	1.26	0.34	0.67
2b	56.1	2.34	2.09	0.45	0.89
Slag tapping hood					
6a	51.5	2.15	2.87	0.67	1.33
6b	52.2	2.26	3.97	0.88	1.76
Controlled blast furnace ventilation gases					
Sanitary baghouse exhaust					
5a	46.1	1.92	2.87	0.75	1.49
5b	41.6	1.73	0.54	0.16	0.31
Slag tapping baghouse exhaust					
7a	51.5	2.15	0.07	0.02	0.03
7b	52.2	2.26	0.08	0.02	0.04
Controlled blast furnace process gases					
Process baghouse					
8a	58.8	2.45	1.81	0.37	0.74
8b	61.5	2.56	0.57	0.11	0.22

[a] Source: Reference 61.
[b] All production rate day calculated from 24-hr daily production quantities.
[c] Estimated from average daily production during test period. Reported daily production inconsistent with operating characteristics.

Total emission rate data were obtained at the smelter refining kettles and casting operation (tests 3 and 4). As previously stated, the calculated emission factors were fairly small compared to other emission sources measured at the plant.

All of the data reported in this test sequence were compiled using standard methodologies but reported in inadequate detail for complete validation. The primary fault lies in the reporting of cubic-spline interpolated size distribution data. Composite size distribution data for blast furnace ventilation gases are presented in Figure 39. Composite size distribution data for controlled and uncontrolled blast furnace emissions are presented in Figure 40. The size-specific emission rate data were given a B test rating. The total mass emission rate data were given an A test rating.

Revere Smelting and Refining (Test 9)

A total of four particulate sampling tests were conducted during the December 1971 testing at the Revere Smelting and Refining secondary lead blast furnace in Newark, New Jersey (Ref. 62,51). Three total mass emission tests were reported for the venturi scrubber and demister controlled blast furnace emissions using an unspecified test method. These tests were given an A rating on the basis of inclusion in the previous AP-42 emission factor which was based only on A-rated data. A fourth mass emission test was reported for the uncontrolled blast furnace emissions. Insufficient and inconsistent production data invalidated the use of these data which were based on the estimate of dry sludge collected over a 10-month period. No particle sizing data were reported.

General Battery Corporation (Test 10)

A total of three particulate sampling tests were conducted during the December 1971 testing at the General Battery Corporation secondary lead blast furnace in Reading, Pennsylvania (Ref. 51,63). Three total emission rate tests were reported for the afterburner, waterspray, baghouse, and venturi scrubber controlled blast furnace using an unspecified test method. These tests were given an A rating on the basis of inclusion in the previous AP-42 emission factor which was based only on A-rated data. No particle sizing data were reported.

Unspecified (Tests 11 to 15 and 22 to 23)

A total of seven particulate sampling tests were conducted at four separate unspecified secondary lead smelters in the Los Angeles Air Pollution Control District (APCD) as reported in February 1972. All tests were conducted in accordance with the Los Angeles APCD's test manual for dust and fume collection. For all tests, process rate data were only reported, although production rates were estimated per Reference 62 (Background Information for Proposed New Source Performance Standards Volume II: Secondary Lead Smelters and Refineries) at 60 percent of process rates (specific data, References 63 and 67 show 83 and 65 percent). All test data

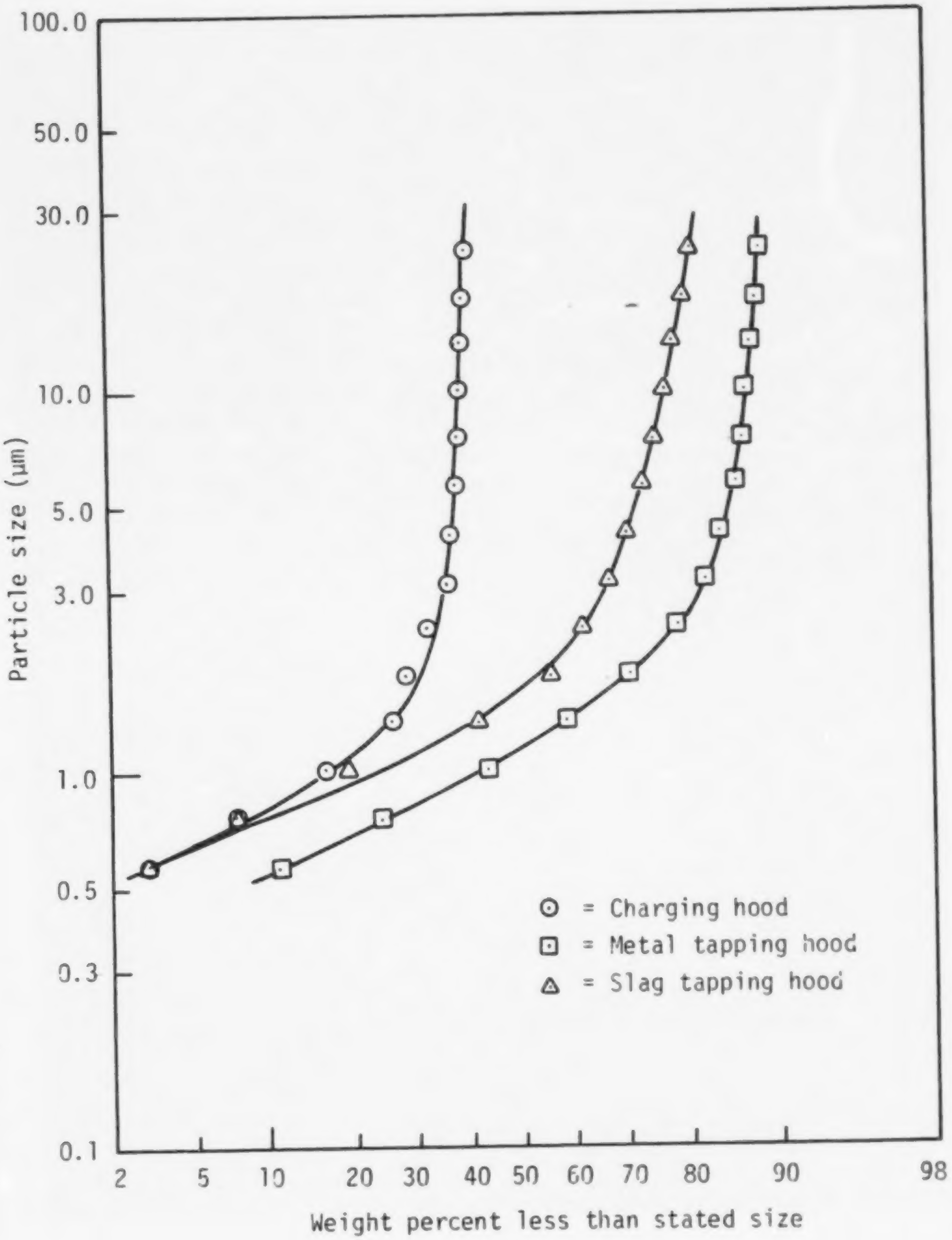

Figure 39. Particle size distribution for uncontrolled emissions from blast furnace ventilation gases.

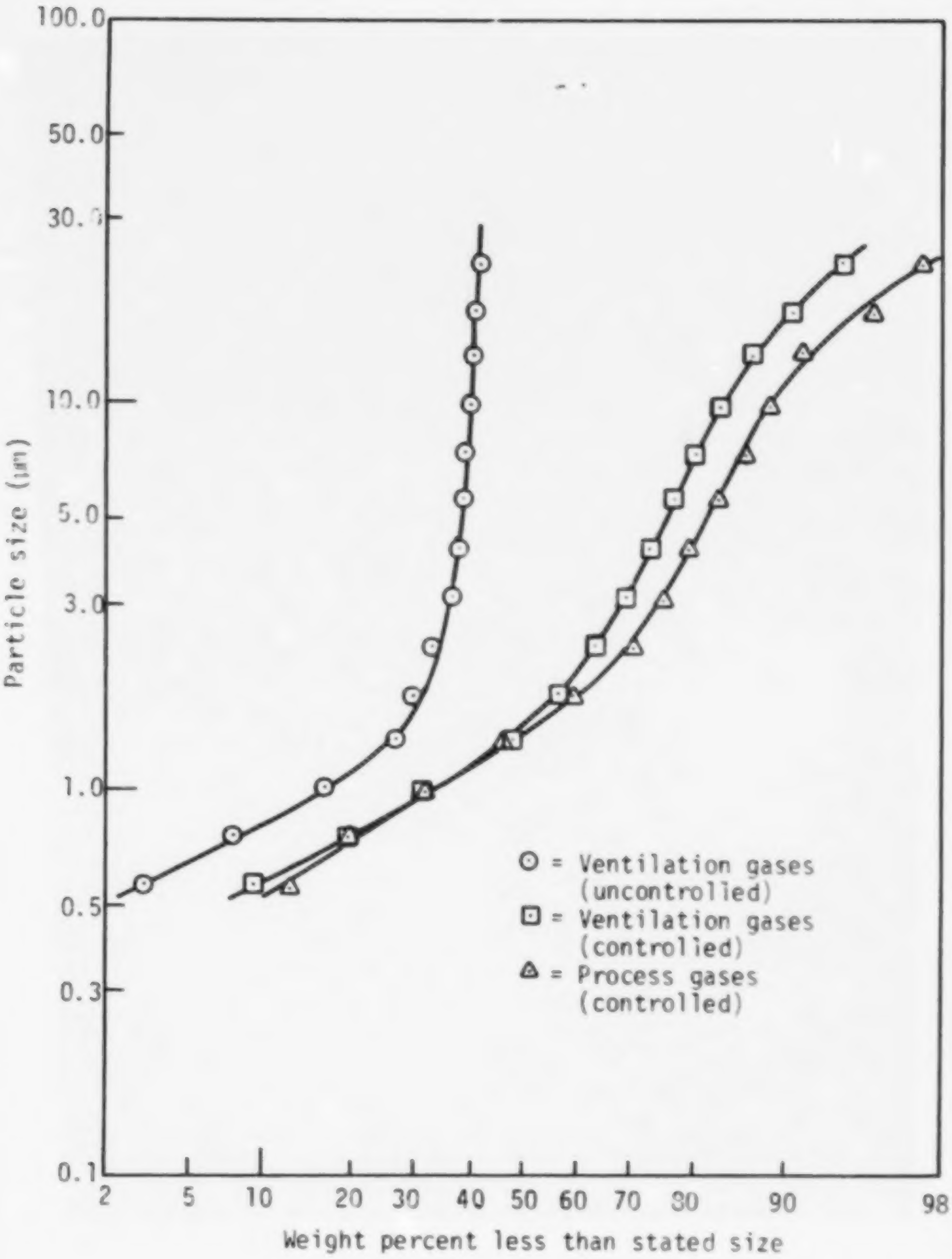

Figure 40. Particle size distribution for uncontrolled and controlled emissions from a blast furnace.

were given an A rating on the basis of inclusion in the previous AP-42 emission factor which was based only on A-rated data.

At the first test site (tests 11 and 12), controlled and uncontrolled total particulate emissions were reported for a blast furnace with an afterburner, cyclone, and baghouse control system.

At the second site (tests 13 and 14), controlled total particulate emissions were reported for a blast furnace with an afterburner and baghouse control system. At this same site, particulate sizing data were reported, but it was not specified whether they were for controlled or uncontrolled emissions. In addition, the data were obtained using micromerograph analysis and, therefore, not necessarily representative of aerodynamic sizing techniques. These data are therefore not reported here.

At the third site (test 15), controlled and uncontrolled total particulate emissions are reported for a reverberatory furnace with a baghouse control system.

N. L. Industries (Tests 16 and 17)

A total of three particulate sampling tests were conducted during the November 1971 testing at the N. L. Industries secondary lead blast furnace in Beech Grove, Indiana (Ref. 51,66). Two total emission rate tests were reported for the cyclone, afterburner, and baghouse controlled blast furnace using an unspecified test method. Three additional total emission rate tests were reported for the uncontrolled blast furnace emissions, however, it was assumed that these represented a single data point. These data were based on total weight of dust collected, and a comparison of emission factors and prodution rate data showed a constant 585 lb/hr (292 kg/Mg) emission rate for all three reported emission factors. These tests were given an A rating on the basis of inclusion in the AP-42 backup file and the designation of a B-rated emission factor in the previous AP-42 section. No particle sizing data were reported.

Quemetco, Inc. (Tests 18 and 19)

A total of four particulate sampling tests were conducted during the January 1972 testing at the Quemetco, Inc. secondary lead reverberatory furnace in Industry, California (Ref. 51,67). Three total emission rate tests were reported for the gravity settler, cyclone, and baghouse controlled reverberatory furnace using an unspecified test method. An additional total emission rate test was reported for the uncontrolled emissions based on the weight of dust collected in the baghouse per shift. These tests were given an A rating on the basis of inclusion in the previous AP-42 emission factor which was based only on A-rated data.

N. L. Industries (Tests 20 and 21)

A total of four particulate sampling tests were conducted during the February 1972 testing at the N. L. Industries secondary lead reverberatory furnace in McCook, Illinois (Ref. 51,68). Three total emission rate tests were reported for the wet cyclone and baghouse controlled reverberatory furnace using an unspecified test method. An additional particulate mass emission test was reported for the uncontrolled exhaust gases based on an unspecified test method. These tests were given an A rating on the basis of inclusion in the previous AP-42 emission factor which was based only on A-rated data. No particle sizing data were reported.

5.2.2 Data Analysis

Emission factors for total and size-specific particulate emissions have been developed for the secondary lead processing industry. The data are generally good, but not necessarily representative of the industry as a whole, with only 10 out of approximately 115 facilities tested. The strength of the data is further limited by the fact that only one of the facilities was tested for particulate size distribution. Most of the size-specific emission factors presented are therefore based on duplicate tests from a single particulate emission source.

Size distributions and size-specific emission factors have been developed for blast furnace process flue gases and associated ventilation gases as presented in Tables 49 and 50, respectively. Figures 46 and 47 represent these data in graphical form. Due to the limited quantity of B-rated test data obtained, a D emission factor rating was assessed. No other size-specific data were located for other emission sources within the industry. The size-specific emission factors were developed directly from complete data, not by applying an industry average size distribution (which was not available) to an industry average particulate mass emission factor. The combined total mass emission factors for controlled blast furnace flue gas and associated ventilation gases as presented in Tables 41 and 42 is 1.41 lb/ton (0.70 kg/Mg) based on limited sampling on low emission source. The industry average figure as presented in Table 51, 2.24 lb/ton (1.12 kg/Mg), does not include associated ventilation gases.

Particulate mass emission factors for controlled and uncontrolled sources within a secondary lead smelter were reevaluated from the previous AP-42 section and are presented in Table 51. A previous presentation of secondary lead emission factors was based on overall process rates. However, it was found that fewer approximations were needed (due to the absence of specific data) if the emission factors were presented on the basis of lead production rates.

Additional primary source data were included and data presented in secondary sources with inadequate references for complete verification removed from the data set. Many of these were determined to be based on engineering estimates and not stack sampling tests. Emission sources found to have verifiable test data were: (1) blast furnaces, (2) reverberatory

TABLE 49. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR BAGHOUSE CONTROLLED EMISSIONS FROM BLAST FURNACE FLUE GASES[a]

EMISSION FACTOR RATING: D

Particle size[c] (μm)	Cumulative mass percent less than stated size	Cumulative emission factors[b] kg/Mg	Cumulative emission factors[b] lb/ton
	Controlled	Controlled	Controlled
15	93.0	0.22	0.45
10	89.0	0.21	0.43
6	83.5	0.20	0.40
2.5	71.0	0.17	0.34
1.25	44.5	0.11	0.21
1.00	33.0	0.08	0.16
0.625	14.5	0.03	0.07
Total	100.0	0.24	0.48

[a] Reference 61.

[b] Based on lead, as produced.

[c] Expressed as aerodynamic equivalent diameter.

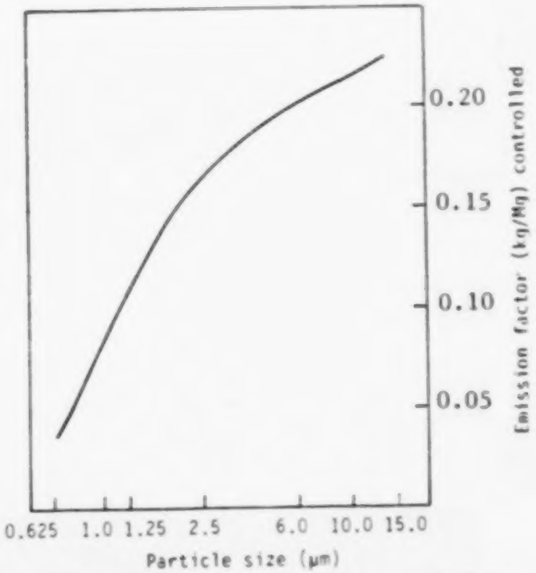

Figure 41. Cumulative emission factors less than stated particle size for baghouse controlled secondary lead processing blast furnace process flue gases.

TABLE 50. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR CONTROLLED AND UNCONTROLLED BLAST FURNACE VENTILATION EMISSIONS[a,b]

EMISSION FACTOR RATING: D

Particle size[d] (µm)	Cumulative mass percent less than stated size		Cumulative emission factors[c]			
			kg/Mg		lb/ton	
	Unctrl	Ctrl	Unctrl	Ctrl[e]	Unctrl	Ctrl[e]
15	40.5	88.5	25.7	0.41	51.4	0.83
10	39.5	83.5	25.1	0.39	50.2	0.78
6	39.0	78.0	24.8	0.36	49.5	0.73
2.5	35.0	65.0	22.2	0.30	44.5	0.61
1.25	23.5	43.5	14.9	0.20	29.8	0.41
1.00	16.5	32.5	10.5	0.15	21.0	0.30
0.625	4.5	13.0	2.9	0.06	5.7	0.12
Total	100.0	100.0	63.5	0.47	127.0	0.94[d]

[a] Reference 61.

[b] Ventilation gases -- include emissions collected from charging, metal and slag tapping ventilation needs.

[c] Based on lead, as produced.

[d] Expressed as aerodynamic equivalent diameter.

[e] Controlled particulate emission factors based on baghouse as control device.

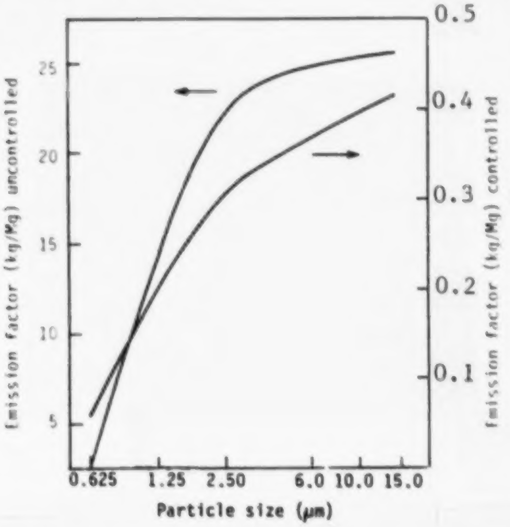

Figure 42. Cumulative emission factors less than stated particle size for controlled and uncontrolled blast furnace ventilation emissions.

furnaces, (3) refining kettles, and (4) casting operations. Although the data obtained for the refining kettles and casting operations did not include controlled emissions (both processes were controlled with a baghouse treating blast furnace ventilation gases), it has been assumed that these emissions are negligible on the basis of an average baghouse control efficiency in excess of 99 percent. Due to the limited quantity of A-rated test data obtained for these emission sources, a C emission factor rating was assessed.

Fugitive emission factors were also assessed for the secondary lead processing industry and are presented in Table 52. The emission factors were determined based on the assumption that particulate and lead emission rates are equal to 5 percent of the uncontrolled stack emission (Ref. 60). Uncontrolled lead emission factors are developed in the following section. Emission factors for sweating furnaces are based on data collected from nonlead secondary nonferrous processing industries. The use of the 5 percent assumption leads to the assessment of an E emission factor rating.

5.3 CHEMICAL CHARACTERIZATION

The chemical composition of particulate emissions from secondary lead smelters is influenced by the scrap material used as feedstock as well as the source location within the plant. Since the majority of lead scrap comes from used batteries, the major constituents are lead and sulfur compounds. The sulfur remains as a residue of battery acids and battery casings containing chlorinated polymers, a major source of chlorine compounds.

Chemical characterization data of point source particulate emissions from secondary lead plants includes both lead content and crystalline species data. Tables 53 and 54 present representative chemical analyses of flue dusts from two secondary lead smelters. Table 55 shows the lead content of particulate emissions from a variety of process locations at one secondary lead smelter.

Previous reporting of particulate lead emission factors has been based on an average 23 percent lead content of particulate emissions. This value was based on a review of six emission tests conducted at secondary lead blast furnaces (Ref. 69). The specific origin of the emitted particulate matter is not clear in that it is not reported whether they result from charging or tapping operations. The specific data shown in Table 55 indicates that these emissions contain approximately 61 percent lead. With approximately 30 percent of blast furnace emissions coming from these operations (Ref. 61), a weighted average of the lead content in uncontrolled blast furnace emissions is 34 percent.

Using the lead content data shown in Table 55, a revised lead emission table can be developed for blast furnaces, kettle refining, and casting and is presented in Table 56.

TABLE 51. PARTICULATE EMISSION FACTOR TABLE -- SECONDARY LEAD PROCESSING[a]

Process	Uncontrolled emissions (kg/Mg)	Uncontrolled emissions (lb/ton)	Emission factor rating	Controlled emissions (kg/Mg)	Controlled emissions (lb/ton)	Emission factor rating
Blast furnace[b]	153 (92-207)	307 (184-413)[c]	C	1.12 (0.11-2.44)	2.24 (0.22-4.88)	C
Reverberatory furnace	162 (87-242)	323 (173-483)	C	0.50 (0.26-0.77)	1.01 (0.53-1.55)	C
Kettle refining	0.02	0.03	C	Neg	Neg[d]	--
Casting operation	0.02	0.04	C	Neg	Neg[d]	--

[a] All emission factors are based on the quantity of lead produced.

[b] Blast furnace emissions are sum of flue gases and associated ventilation gases from charging and tapping.

[c] Figures in parentheses are range of emission factors obtained.

[d] Emission factor determined to be negligible on the basis of an average baghouse control efficiency in excess of 99 percent.

TABLE 52. FUGITIVE EMISSION FACTORS FOR SECONDARY LEAD PROCESSING[a]

EMISSION FACTOR RATING: D

	Particulate matter		Lead	
Emission source	(kg/Mg)	(lb/ton)	(kg/Mg)	(lb/ton)
Sweating	0.8 to 1.8	1.6 to 3.5[b]	0.2 to 0.9	0.4 to 1.8[c]
Smelting	4.3 to 12.1	8.7 to 24.2	0.88 to 3.5	1.75 to 7.0[d]
Kettle refining	0.001	0.002	0.0003	0.0006[d]
Casting	0.001	0.002	0.0004	0.0007[d]

[a] Based on an engineering estimate that fugitive emissions equal 5 percent of the uncontrolled stack emissions. All factors are based on the amount of lead product, except for sweating which is based on the quantity of material charged to the furnace, Reference 51.

[b] Based on sweating furnace emissions from nonlead secondary nonferrous processing industries, Reference 55.

[c] Emission factor based on 23 percent lead content of uncontrolled blast furnace flue emissions, References 47 and 58.

[d] Reference 66.

TABLE 53. CRYSTALLINE SPECIES PRESENT IN FLUE DUST FROM A SECONDARY LEAD SMELTER (BY X-RAY DIFFRACTION)[a]

Plant	PbS	Pb	$PbSO_4$	$PbCl_2$	$PbO \cdot PbCl_2$ Solid solution
East Penn	Major	Moderate to trace	Moderate to minor	--	Moderate to minor
General Battery	--	--	--	Major	--

[a] Source: Reference 61.

TABLE 54. CHEMICAL COMPOSITION OF FLUE DUST FROM A SECONDARY LEAD SMELTER[a]

Plant	Percent		
	Pb	Cl	K
East Penn	64 to 99	1 to 3	0.3
General Battery	53	8.5	1.3

[a] Source: Reference 61

TABLE 55. LEAD CONTENT OF PARTICULATE EMISSIONS FROM SECONDARY LEAD SMELTING AND REFINING[a]

Process	Lead content (percent by weight)
Blast furnace (uncontrolled)	
Ventilation gases	
Charging	61.1
Metal tapping	49.6
Slag tapping	58.7
Weighted average[b]	61.0
Flue gases[c]	23.0
Average (ventilation and flue)[d]	34.0
Blast furnace (controlled)	
Ventilation gases	22.3
Flue gases	33.2
Average (ventilation and flue)[b]	26.1
Kettle refining	39.7
Casting	36.1

[a] Source: Reference 61 except where noted.
[b] Weighted average based on emission factors.
[c] Average of six tests reviewed in Reference 69.
[d] Based on 30 percent of total blast furnace emissions from ventilation system.

TABLE 56. LEAD EMISSION FACTOR TABLE -- SECONDARY LEAD SMELTING AND REFINING[a]

Process	Uncontrolled emissions		Emission factor rating	Controlled emissions		Emission factor rating
	(kg/Mg)	(lb/ton)		(kg/Mg)	(lb/ton)	
Blast furnace[b]	52 (31-70)	104 (63-140)[c]	C	0.15 (0.02-0.32)	0.29 (0.03-0.64)	C
Reverberatory furnace	32 (17-48)[e]	65 (35-97)	--	NA	NA[d]	--
Kettle refining	0.006	0.012	C	Neg	Neg[f]	--
Casting operation	0.007	0.014	C	Neg	Neg	--

[a] Emission factors based on ton of lead product.
[b] Blast furnace emissions are sum of flue gases and associated ventilation hoods (charging and tapping).
[c] Figures in parentheses are range of emission factors obtained.
[d] NA -- Not available.
[e] Based on an estimated 20 percent lead content for uncontrolled reverberatory furnace flue emissions as stated in previous AP-42 section on secondary lead processing.
[f] Emission factor determined to be negligible on the basis of an average baghouse control efficiency in excess of 99 percent.

SECTION 6

PRIMARY ZINC PROCESSING

6.1 OVERVIEW*

This section is a source category report for particulate matter emissions from the primary zinc industry. This section includes a description of the primary zinc industry and the various processes involved in primary zinc production. Sources of particulate matter emissions from zinc processing are discussed, as well as the type of particulate matter emission control equipment used by the industry for each process. Information concerning particulate matter emission rates and associated particle size distributions for the zinc production processes, is summarized and reviewed. Size-specific emission factors are then developed, from this data, and rated according to the criteria outlined in Section 1. Finally, a revised AP-42 section on the zinc processing industry is included.

Zinc is fourth among metals in annual worldwide consumption, being surpassed only by steel, aluminum, and copper. It is exceedingly versatile and useful, with a significant portion being used in automobiles and construction as die castings, in brass, as a protective coating for steel, and as a chemical compound in rubber and paints.

Zinc deposits in the United States are found from Maine southward through the Appalachian Mountains, and west through the Mississippi Valley into the Rocky Mountain States. Reserves are estimated at 16.5 million tons (15 Tg) of zinc. Reserves containing only zinc account for about two-thirds of the zinc in domestic reserves; extraction of the remaining one-third is dependent to some degree on the recovery of one or more coproducts or byproducts. Cadmium (Cd), thallium (Tl), indium (In), and germanium (Ge) are produced only as a byproduct of zinc production, and lead is the major coproduct.

A forecast was made of the possible demand for zinc in the United States in the year 2000 (Ref. 70). The forecasted domestic demand ranges from 1.2 to 2.5 million tons (1.1 to 2.3 Tg) compared with 1.1 million tons (1.05 Tg) used in 1981. The most probable demand, 1.8 million tons (1.6 Tg), represents an average annual growth rate of 2.2 percent over current usage.

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*Much of this description is abstracted from Reference 70

United States reserves are insufficient to meet even the low forecast of probable cumulative primary demand of 21 million tons (19 Tg). Although some deposits currently classified as resources are expected to become reserves during the forecast period, the United States is expected to continue to rely on imports for a significant portion of its supply.

During the period 1968 to 1982, the United States went from a position of near self-sufficiency in metal production to one requiring large metal imports. U.S. smelting capacity declined by about 60 percent from 1968 to 1982 despite the construction of two new plants.

In 1979, there were seven facilities producing slab zinc in the United states (Ref. 58 and 70). Two of these plants, the Bunker Hill Co. electrolytic zinc plant in Kellogg, Idaho, and the New Jersey Zinc Co. vertical retort zinc plant in Palmerton, Pennsylvania, have shut down, and no longer produce slab zinc, although the Bunker Hill plant could be reopened. In addition to these, the St. Joe Minerals Corp. vertical retort was shut down temporarily in December 1979 and reopened at reduced capacity in late 1980. Plants were closed because they were obsolete, could not meet environmental standards, could not obtain sufficient concentrate feed, or for some combination of these reasons. All three plants that have closed their operations since 1979 were built prior to 1930, and two of the three used the vertical retort smelting process. These plants produce approximately two and a half times more particulate emissions per ton of zinc produced than plants using the electrolytic process.

Several large, vertically integrated firms with mines, smelters, and refineries are prominent in the U.S. primary zinc industry. The principal companies that operated both mines and smelters or refineries in 1981 were Amax Zinc Co., Inc., ASARCO Incorporated, The Bunker Hill Co., Jersey Miniere Zinc Co., and St. Joe Zinc Co. In 1981 these five companies accounted for over 86 percent of the primary slab zinc produced in the United States and 58 percent of the mine output. After 1979, when the three largest smelters were either shut down or operating at reduced capacity, the industry is a little more evenly balanced. The five remaining companies (including National Zinc, a custom producer of slab zinc) have an average capacity of 84,000 tons (76,000 Mg), with no single company dominating the field. Table 57 presents a list of the current primary slab zinc processing companies.

During the forecast period to 2000, United States dependence on metal imports is expected to remain between 40 and 60 percent. Increased demand may be generated by government buying to attain the stockpile goal. Several shifts in the zinc demand pattern are foreseen through 2000. Much less zinc will be used in die casting for automobiles because of substitution of other materials. Galvanizing will become a major use as more galvanized steel is used in residential construction and automobiles. After about 1990 zinc batteries for automobile propulsion and electrical load leveling may become important, resulting in increasing demand for zinc compounds. Much of current zinc consumption is for dissipative uses, and therefore secondary metal provides only a small part of the total supply. However, recovery of

TABLE 57. PRIMARY ZINC PROCESSING CAPACITY[a] -- 1983

Operator	Location	Type of plant	Slab zinc capacity (tons)	Slab zinc capacity (Mg)
Amax Zinc	Sauget, IL	Electrolytic	84,000	76,000
ASARCO	Corpus Christi, TX	Electrolytic	99,000	90,000
Jersey Miniere Zinc	Clarksville, TN	Electrolytic	90,000	82,000
National Zinc	Bartlesville, OK	Electrolytic	56,000	51,000
St. Joe Zinc[b]	Monaca, PA	Electrothermic	89,000	81,000

[a] Primary zinc capacity for slab zinc only. Zinc oxide commonly referred to as secondary even if process feedstock is zinc ore (Ref. 58 and 70).
[b] Original plant capacity 222,000 tons (201,000 Mg). The plant was shut down in December 1979 and reopened in late 1980 at reduced capacity. Electric furnace addition in 1982 and 1983 increased annual capacity from 68,000 tons to 77,000 tons to 81,000 tons (Ref. 58).

secondary zinc is likely to increase, especially if zinc batteries from electric vehicles become a major source of zinc scrap beyond 1995.

6.1.1 Primary Zinc Process*

The production of slab zinc from source ores is accomplished in the U.S. by two major processes, as shown in Figure 43. Four of the five slab zinc smelters use the electrolytic process, while the fifth uses an electrothermic procedure. Both processes are basically initiated by two similar steps. The first step involves roasting the ore concentrate to remove sulfur(s) and forming an impure zinc oxide (ZnO) material called calcine. Subsequent to this, the calcine is converted to slab zinc (Zn) by either a thermochemical reduction process (sintering and retorting), or electrolysis.

Roasting

Roasting is a high-temperature process that removes S from zinc ore concentrate and produces the calcine product. Roasting may be accomplished by any of three types of facilities: (1) multiple hearth, (2) suspension,

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*Much of the following description is abstracted from Reference 48.

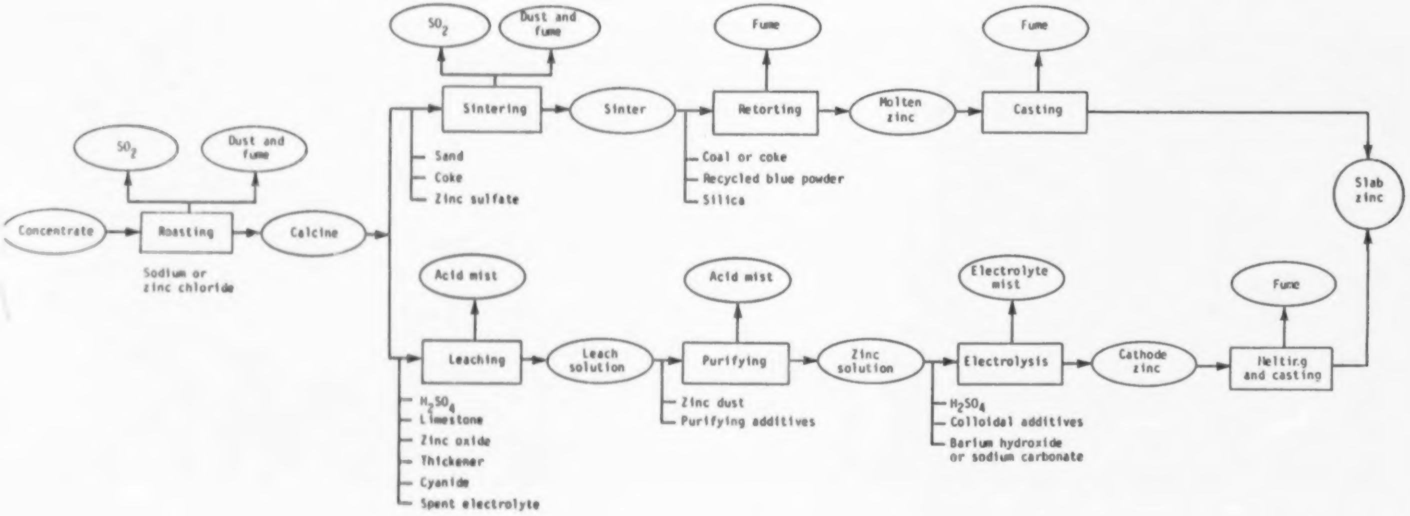

Concentrate
Roasting
Sodium or zinc chloride
SO_2
Dust and fume
Calcine
Sintering
SO_2
Dust and fume
Sand
Coke
Zinc sulfate
Sinter
Retorting
Fume
Coal or coke
Recycled blue powder
Silica
Molten zinc
Casting
Fume
Slab zinc
Leaching
Acid mist
H_2SO_4
Limestone
Zinc oxide
Thickener
Cyanide
Spent electrolyte
Leach solution
Purifying
Acid mist
Zinc dust
Purifying additives
Zinc solution
Electrolysis
Electrolyte mist
H_2SO_4
Colloidal additives
Barium hydroxide or sodium carbonate
Cathode zinc
Melting and casting
Fume

Figure 43. Primary zinc processing schematic.

and (3) fluidized-bed. Multiple hearth roasters are the oldest type of roaster used in the United States. As stated in the previous section, however, many of the older plants are either being phased out, or renovated. The major advantage of the fluidization roaster is its ability to process higher tonnages per furnace per unit time, because of the increased reaction rates for desulfurization. Also, like the suspension roaster, the fluidized-bed roaster can produce a calcine with lower total S content than the multiple hearth processes.

In a multiple hearth roaster, the concentrates drop from hearth to hearth. As much as 20 percent of the Cd present in the zinc concentrate may be vaporized. Any mercury (Hg) present is volatilized and enters the gas stream. The roaster consists of a brick-lined cylindrical steel column with nine or more hearths. A motor-driven central shaft has two rabble arms attached for each hearth, as well as cooling pipes. First, the concentrates enter at the top of the roaster and are dried in an upper hearth. The central shaft rotates slowly, raking the concentrates over the hearth with the rabble arms, gradually moving them to the center and a drop hole to the second hearth. They move across this second hearth to a slot near the outer edge, where they drop to the third hearth. The concentrates continue down through the roaster in this spiral fashion and are discharged at the bottom. Additional fuel must be added to maintain combustion.

The low production rates are a major disadvantage of multiple hearth roasting. However, since less dust is carried away in the exhaust gas stream, more volatile sulfides such as cadmium sulfide (CdS) are removed preferentially. This is helpful when Cd is recovered from the flue dust, since there is less zinc dust contamination.

Suspension, or flash roasting is a process used for the rapid removal of S and the conversion of zinc to calcine. In this processing procedure the concentrates are allowed to fall through a heated oxidizing atmosphere or are blown into a combustion chamber for reaction. Roasting in suspension promotes better heat transfer than multiple hearth roasting and thereby increases reaction rates for desulfurization. The reaction usually proceeds without the addition of fuel unless the zinc sulfide (ZnS) content of the ore is too low.

A suspension roaster consists of a refractory-lined cylindrical steel shell with a large combustion space at the top and two to four hearths in the lower portion, similar to those of a multiple hearth furnace. The feed must be carefully sized, therefore additional grinding may be needed for proper preparation. In more recent flash furnace models, concentrate is introduced into the lower one or two hearths to dry before final grinding in an auxiliary ball mill and introduction into the combustion chamber.

About 40 percent of the roasted product settles out on a collecting hearth at the bottom of the combustion chamber. This coarser material is likely to contain the most S, so it is further desulfurized by being rabbled across this hearth and another hearth immediately below before being discharged from the roaster. Particulate collected in ducts and control devices can be fed to these hearths to achieve further oxidation and sulfate decomposition or to obtain a more homogeneous product. The remaining 60 percent of the product leaves the furnace with the flue gases.

The fluidized-bed roaster is the newest method for removing S and converting zinc to calcine. In this roaster, finely ground sulfide concentrates are suspended and oxidized in a bed supported on an air column. As in the suspension roaster, the reaction rates for desulfurization are more rapid than in the older multiple hearth processes. The fluidized-bed roaster was originally designed for calcining arsenopyrite gold ores; several North American zinc smelters have adopted it in different forms for use in pyrometallurgical and electrolytic processes. Designs differ primarily in whether the roasters are charged with a wet slurry or a dry charge. The S content of the charge to a fluidized-bed roaster is typically reduced from about 32 to 0.3 percent. At the St. Joe electrothermic plant, a very low S content calcine is supplied to the electric retort by using a multiple hearth roaster preceeding the fluidized bed roaster.

In the fluidized-bed process, no additional fuel is required after ignition has been achieved and operation of the system is continuous. The feed enters the furnace and becomes fluidized, or suspended, in a bed supported on an air column. Temperature control is achieved manually or automatically, via water injection. Relatively low, uniform operating temperatures appear to lessen the formation of ferrite. The temperatures in the roaster are high enough to warrant the use of waste heat boilers to cool the off-gases.

In a zinc smelter, the roasting process is typically responsible for more than 90 percent of the potential sulfur dioxide (SO_2) emissions; 93 to 97 percent of the S in the feed is emitted as sulfur oxides. Concentrations of SO_2 in the off-gas vary with the roasting operation. Because concentrations of SO_2 produced during roasting are high enough to allow recovery of sulfuric acid in an acid plant, this process has become a normal part of zinc production. Typical SO_2 concentrations for a multiple hearth furnace range from 4.5 to 6.5 percent (Ref. 6). The SO_2 concentration in the off-gas from suspension roasting is higher than that in multiple hearth processes, averaging 10 to 13 percent (Ref. 51). The SO_2 content of fluid-bed roaster gas is reported to be 7 to 12 percent.

In roasting, if enough sulfur is originally present as sulfide, the operation becomes autogenous. For pyrometallurgical refining, zinc sulfate ($ZnSO_4$) must be removed. The following reactions occur during roasting:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \qquad (1)$$

$$2SO_2 + O_2 \rightarrow 2SO_3 \qquad (2)$$

$$ZnO + SO_3 \rightarrow ZnSO_4 \qquad (3)$$

In pyrometallurgical reduction only the oxide state is desired, whereas in electrolytic reduction, small amounts of the sulfate state are acceptable.

Sintering and Retorting

The pyrometallurgical reduction of calcine to slab zinc occurs in a two step process involving sintering and either vertical or electrical retorting. Sintering has two purposes: first, to volatilize lead and cadmium impurities and discharge them into the off-gas stream where they can be captured; and second, to agglomerate the charge into a hard, permeable mass suitable for feed to a pyrometallurgical reduction system. Retorting is a continuous reduction and volatilization process for producing high-purity zinc from zinc oxide by reaction with carbon at elevated temperatures.

In the sintering step, the Dwight-Lloyd-type sinter machines are typically used. These are downdraft units in which grated pellets are joined to form a continuous conveyor system. The feed is normally a mixture of calcine or concentrates, recycled ground sinter, and the required amount of carbonaceous fuel, which is pelletized and sized to assure a uniform, permeable bed for sintering before it is fed to the machines and ignited. The sintering operation is a source of SO_2. The SO_2 concentration in off-gas from the sinter machine is very low, 0.1 to 2.4 percent by volume, which represents only 1 to 5 percent of the sulfur originally present in the feed (Ref. 71). When zinc calcines are sintered, sulfur emissions from a sinter machine are primarily determined by the S content of the input calcine, although some emissions result from the $ZnSO_4$ liquor added to the sinter mix.

In the retorting step, because of the relatively low boiling point of zinc, 1,663°F (906°C), reduction and purification of zinc-bearing minerals can be accomplished to a greater extent than with most minerals. The ZnO feed is reduced and then immediately separated from its nonvolatile impurities (reaction 4) in a high temperature reducing environment produced by an external heat source, and the carbon monoxide (CO) regeneration reaction (reaction 5).

$$ZnO + CO \rightarrow Zn(vapor) + CO_2 \qquad (4)$$

$$CO_2 + 0 \rightarrow 2\ CO \qquad (5)$$

The zinc vapor and CO produced pass from the main furnace to a condenser, where zinc is recovered by being bubbled through a molten zinc bath.

The smelting reduction of ZnO to metallic zinc can be accomplished in either a horizontal or vertical pyrometallurgical retort or in a electrothermic retort furnace. The latter system, also referred to as an electric retort, is the only thermochemical smelting process currently in use in the United States. The electrothermic furnace has a number of advantages over other pyrometallurgical processes. First, the increased thermal efficiency (compared with external heating methods) results in cost savings in fuel consumption. Larger quantities of charge can be treated, and the continuous operation is amenable to automation. The furnace can readily process secondary zinc scrap and zinc residues. Because of special deleading by heat treatment in multiple-hearth roasters followed by desulfurization in fluidized-bed roasters, electrothermic furnaces emit practically no SO_2 or particulates.

The St. Joe electrothermic furnaces are vertical, refractory-lined cylinders. The largest furnaces now in use have an inside diameter of 5 ft (1.5m) and are 50 ft (15m) high, with a production capacity of about 100 tons (90 Mg) per day (Ref. 6). Graphite electrodes protrude into the shaft, and the reaction heat is generated from the resistance of the furnace charges to the current flow between the electrodes. Eight pairs of electrodes introduce power into the furnace. Each top electrode has a mate near the bottom.

Preheated coke and sinter, along with miscellaneous minor zinc-bearing products such as "blue powder," are fed continuously into the top of the furnace from a rotary feeder. Gravity moves the charge downward through the shaft. Unlike other retorting processes, an unusually hard sinter is required to maintain strength and porosity in the tall columns, even after most of the zinc content has been removed. Silica is usually added to the sinter mix to increase its structural strength. The coke serves as the principal electrical conductor, carrying the alternating current between each top electrode and the bottom electrode on the opposite side. The heat developed provides the energy required for smelting.

The St. Joe electrothermic furnaces operate at atmospheric pressure. Internal temperatures are 2,600°F (1,400°C) at the axis of the furnace, 2,200°F (1,200°C) in the main body of the charge, and 1,650°F (900°C) near the wall. A vacuum of 6 to 10 in. (15 to 25 cm) of mercury is applied to the outlet of the condenser, causing the vapor/gas mixture to be drawn through it in large bubbles. Water-cooled hairpin loops at the condenser cooling well maintain a constant batch temperature of 900° to 930°F (480° to 500°C). Temperatures for purification steps vary, since separation is based on differences in boiling points.

Electrolysis

Electrolytic production of zinc is the other major process by which primary zinc is processed. The first step is to separate zinc from gangue minerals by leaching roasted calcine in a recycled electrolyte solution. The zinc dissolves, and the insoluble gangue is separated from the solution by decantation, thickening, and filtration. The solution is purified in the second step, and the waste solids are either discarded or, if their concentration warrants, further processed to recover lead and precious metals. In the third step, electrolysis, metallic zinc is recovered from the purified solution by passing a current through an electrolyte solution, causing zinc metal to deposit on a cathode.

Two general leaching methods can be employed, described as either a single or a double leach. In a single leach, recycled electrolyte, which is a solution containing principally sulfuric acid (H_2SO_4) is brought only once in contact with the calcine. ZnO in the calcine reacts with H_2SO_4 to form soluble $ZnSO_4$ and water (reaction 6).

$$ZnO + H2SO_4 \rightarrow Zn^{+2}_{(aq)} + SO_4{}^{-2}_{(aq)} + H_2O \qquad (6)$$

The single leach is not often practiced, however, since losses of H_2SO_4 are excessive and recovery of zinc is poor.

Double leaching is used most often. In several variations, the calcine is leached first in a solution that is neutral or slightly alkaline, then in an acidic solution, with the liquid passing countercurrently to the flow of calcine. In the neutral leach, the readily soluble sulfates from the calcine dissolve, but only a portion of the ZnO enters into solution. The second acidic leach solubilizes the remainder of the ZnO, but also dissolves many impurities, especially iron (Fe). Recycling the liquor to the first neutral stage causes much of the iron to reprecipitate, so the neutral leach acts also as an initial stage of solution purification. In some of the more complex process variations, considerable overlap occurs between leaching and purification steps, and the calcine may be subjected to as many as four leaching operations in progressively stronger or hotter acids to bring as much of the zinc as possible into solution.

The leaching of zinc calcine causes other elements in addition to zinc to dissolve. Unless impurities are removed from the solution, they will either contaminate the zinc product or interfere with the proper operation of the electrolysis process. The solution from leaching is therefore purified to remove metallic ions that are more electropositive than zinc.

Purification is usually conducted in large agitated tanks. A variety of reagents is added in a sequence of steps that cause impurities to precipitate. The precipitates are separated from the solution by filtration. The purification techniques are among the most advanced applications of inorganic solution chemistry in industrial use, and vary from one smelter to another. Fe is often removed in conjunction with the leaching process by precipitation as a hydrated oxide (goethite) or a complex sulfate (jarosite). Some of these processes, which are patented, also reduce the concentration of arsenic (As) and other elements. Almost all smelters then add zinc dust, often in the form of "blue powder" from the pyrometallurgical production of zinc. This addition causes a cementation reaction that precipitates Cd, copper (Cu), and several other elements. The final steps remove all but trace quantities of a group of metals that includes As, antimony (Sb), cobalt

(Co), germanium (Ge), nickel (Ni), and Thallium (Tl). These metals severely interfere with electrolytic deposition of zinc, and their final dissolved concentrations are limited usually to less than 4 x 10^{-7} lb/gal (0.05 mg/liter). Electrolysis takes place in rectangular tanks, or cells, each of which holds a number of closely spaced rectangular metal plates. Alternate plates are made of lead containing 0.75 to 1.0 percent silver; these are the anodes that are electrically connected to a positive potential. The remaining plates are made of aluminum, and are connected with a negative electrical potential. Purified electrolyte is circulated slowly through the cells, and water in the electrolyte dissociates, releasing oxygen at the anode. Electrode voltage is maintained sufficiently high so hydrogen gas is not released at the cathode; instead, zinc ions absorb electrons and deposit zinc metal. Hydrogen ions remain in solution, and thereby regenerate sulfuric acid for recycle to the leach process. The reaction sequence involved in electrolytic production of zinc is shown below in reactions 7 through 9.

$$2H_2O \xrightarrow[\text{anode}]{H_2SO_4} 4H_{(aq)} + 4e^- + O_2 \qquad (7)$$

$$2Zn^{+2}_{(aq)} + 4e^- \xrightarrow{\text{cathode}} 2Zn \qquad (8)$$

$$4H^+_{(aq)} + 2SO4^{-2}_{(aq)} \longrightarrow 2H_2SO_4 \qquad (9)$$

Zinc smelters contain a large number of electrolytic cells, often several hundred. They are most often made of concrete with a lead, plastic, or vitreous lining, and are electrically connected in series blanks. A portion of the electrical energy is converted into heat, which increases the temperature of the electrolyte. Therefore, a portion of the electrolyte is continuously circulated through cooling towers. These are usually open towers, in which the electrolyte falls through a rising stream of air drawn through the tower by fans. This method both cools the electrolyte and evaporates the excess water. The cooled and concentrated electrolyte is repumped into the cells.

Every 24 to 48 hr, each cell is shut down and the zinc-coated cathodes are removed, rinsed, and the zinc is mechanically stripped from the aluminum plates. Stripping is accomplished manually in some smelters, while others use specialized automated equipment. The aluminum cathodes are then chemically cleaned, replaced in the cells, and the cell is restored to normal operation.

Casting

The final process in primary zinc processing is the casting of zinc slabs. Pyrometallurugical zinc is already in a molten state, and can therefore be cast directly. Electrolytic zinc however must first be melted in either reverberatory or electrolytic furnaces. Ammonium chloride (NH_4Cl) flux is often added to retard surface oxidation in melting and alloying kettles. Various alloys, such as galvanizing zinc, are formed during the final stages before casting into either 60 lb (27 kg) slabs or larger 1,400 to 2,400 lb (640 to 1,100 kg) slabs.

6.1.2 Particulate Emission Sources

Particulate emissions from the slab zinc processing industry come predominantly from roasters, with additional emissions originating from sintering and electric retort furnaces. Particulate emissions are negligible from electrolysis plants, except for the preliminary roasting which is common to both pyrometallurgical and electrolytic plants.

Particulate emissions from roasters in the form of dust and fume depend on the type of facility used. Emissions from multiple hearth roasters are estimated as 5 to 15 percent of feed (Ref. 72). Emissions are similarly estimated at 60 and 70 percent of product calcine respectively for suspension and fluidized-bed roasters (Ref. 22). Fugitive particulate emissions are negligible from all types of roasters.

Pyrometallurgical reduction and casting are the only other sources of particulate emissions at a slab zinc processing plant. Sintering represents the second largest source of particulate emissions. Both point source and fugitive particulates in the form of dust and fume are released by a zinc sinter plant. Electric retort furnaces similarly produce point source and fugitive particulate emissions. Melting and alloying furnaces and casting are a source of fugitive particulate emissions in the form of metal and metallic oxide fume.

6.1.3 Particulate Emission Controls

The control of particulate emissions is a standard practice in the zinc processing industry. Efficient particulate control is crucial to the economic operation of a zinc smelting facility. The industry uses typical particulate control technology, including waste heat boilers, cyclones, ESP's, baghouses, and impingement scrubbers.

Particulate control at a roasting plant is generally achieved using ESP's. Suspension and fluidized-bed roasters, which have emission rates of around 60 to 70 percent of calcine product, use waste heat boilers and cyclones to reduce the dust loading of the exhaust gas entering the ESP. At a suspension roaster, 60 percent of the product leaves the furnace with the gas stream, passing first through a waste heat boiler and then to cyclones and an ESP, where it is recovered. About 20 percent of the suspended dust drops out in the boiler: the cyclones and precipitator remove about 99.5

percent of the remainder (Ref. 22 ,. Testing at one fluidized-bed roaster processing 140 tons (127 Mg) of dry concentrates per day, indicated that 30 percent of the calcine left the roaster via the overflow pipe, 23 percent was deposited in the waste heat boiler, 44 percent was captured by the cyclones, and 3 percent entered the ESP with the flue gases (Ref. 22).

Particulate emissions at sinter plants are controlled by water spray and air injection cooling followed by a combination of cyclones, ESP's, and baghouses. Particulate control at an electric retort furnace is achieved by using a high-velocity impingement scrubber.

6.2 PRIMARY ZINC PROCESSING EMISSION FACTORS

The following subsection outlines the methodology involved in the development of size-specific emission factors for various processes within the primary zinc industry. The data from which the emission factors are developed are reviewed, analyzed, and rated according to the guidelines established in the document "Technical Procedures for Developing AP-42 Emission Factors and preparing AP-42 Sections."

6.2.1 Data Review

Total and size-specific particulate emissions data have been obtained from three emission tests at primary zinc processing plants. Table 58 presents a summary of these tests, showing (where available) test site, emission source, control device, the type of data obtained, and the quality of the data.

TABLE 58. SUMMARY OF PARTICULATE EMISSIONS TESTS -- PRIMARY ZINC PROCESSING

Test no.	Source location	Emission point	Control device(s)	Type of data[a]	Rating	Reference
1	New Jersey Zinc Co.	Retort furnace	--	1	A	73
2	New Jersey Zinc Co.	Sinter plant	Cyclone	1	A	73
3	New Jersey Zinc Co.	Sinter plant	Cyclone and ESP	1	A	73

[a] 1 -- Particle size distribution.

Total particulate emissions data referenced in the previous AP-42 section were reviewed where available. Much of this data was determined to be based on engineering judgment and estimates. Where possible, these estimates were replaced by the data presented below. The data and estimates used to determine the new emission factors are presented in Table 59. Original AP-42 data are presented without any changes in this table.

Total fugitive particulate emission factors were estimated from a variety of similar operations in both the ferrous and nonferrous smelting industries. These estimated emission factors are presented directly in Table 60.

Size-specific emission test data were obtained for sinter plants and vertical retort furnaces. None of these tests were reported in adequate detail to determine size distributions without making substantial assumptions; consequently, they were not reported. No size distribution tests were located for fugitive emissions.

New Jersey Zinc Co. (Not Included)

A total of three particulate size distribution sampling tests were conducted at one of nine vertical retorts during the March 1974 testing at the New Jersey Zinc Co. primary zinc smelter in Palmerton, Pennsylvania, as reported in the EPA Environmental Assessment Data System (EADS): FPEIS Test Series 44 (Ref. 74). (The same tests are apparently also reported in Ref. 73) Of these tests, only two were obtained during normal operating conditions. The third was obtained during a retort blow-out. The tests were conducted using EPA methods and one Andersen cascade impactor with a cyclone precutter. The data were reported as particulate loading at the respective stage calculated mean aerodynamic diameter. Although total particulate grain loading data were provided for both tests, the sum of the incremental size-specific particulate loading data was not consistent with the values obtained. Only by making the assumption that the unaccounted mass should be associated with a back-up filter could a size distribution be obtained. Doing this resulted in an average size distribution with approximately 80 percent of the particulate emissions less the 2 μm. However, a similar study (Ref. 73) performed at the same plant and possibly the same actual tests (the reference in the EADS report is insufficient to determine this, although some of the process type data are identical) reports only 70 percent less than 2 μm.

An additional constraint to the use of these data is uncertainty in the particulate emission roles calculated from the data presented. EADS test series an average total particulate emission rate of 64.3 lb/hr (29.2 kg/hr) as calculated from exhaust stream total particulate loadings of 0.188 gr/dscf and 0.190 gr/dscf (0.431 g/nm^3 and 0.435 g/nm^3) and stack volumetric flowrates of 38,600 scfm and 40,700 scfm (18.2 nm^3/s and 19.2 nm^3/s) for the two tests. The data presented in the other study at this plant shows total particulate emission rates of 6.7 lb/hr (3.03 kg/hr). The order of magnitude discrepancy between the values leads to a high degree of uncertainty concerning the overall quality of the data as reported.

TABLE 59. TOTAL PARTICULATE EMISSION FACTOR DATA AND ESTIMATES -- PRIMARY SLAB ZINC PROCESSING[a]

Process	Uncontrolled emissions (lb/ton)	Uncontrolled emissions (kg/Mg)	Emission factor rating	Controlled emissions (kg/Mg)	Controlled emissions (lb/ton)	Emission factor rating
Roasting						
Multiple hearth	333[b]	167	E	NA[n]	NA	--
Multiple hearth	120[c]	60	B	NA	NA	--
Suspension[d]	2,000	1,000	E	4	8	E
Fluidized-bed	2,000[e]	1,000	E	NA	NA	--
Fluidized-bed	2,333[f]	1,167		NA	NA	--
Sinter Plant						
Without controls	125[g]	62.5	E	--	--	--
Without controls	90[h]	45.0	B	--	--	--
With cyclone	--	--	--	24.1	48.2[i]	D
With cyclone and ESP	--	--	--	8.25	16.5[i]	D
Vertical retort	14.3[j]	7.15	D	NA	NA	--
Vertical retort	100.0[k]	50.0	B	NA	NA	--
Electric retort	20.0[l]	10.0	E	NA	NA	--
Electrolytic process	6.6[m]	3.3	B	NA	NA	--

[a] All emission factors based on quantity of slab zinc produced.

[b] Estimated on the basis of an average 10 percent of feed released as particulate emissions and a zinc production rate at 60 percent of roaster feedrate. Reference 73.

[c] AP-42 data. Reference 75.

[d] Estimated on the basis of an average 60 percent of feed released as particulate emission and a zinc production rate at 60 percent of roaster feedrate. Controlled emissions based on 20 percent drop-out in waste heat boiler and 99.5 percent drop-out in cyclone and ESP. References 22 and 76.

[e] Estimated on the basis of an average 60 percent of feed released as particulate emissions and a zinc production rate of 60 percent of roaster feedrate. Reference 76.

[f] Estimated on the basis of an average 70 percent of feed released as particulate emissions and a zinc production rate of 60 percent of roaster feedrate. Reference 22.

[g] Based on unspecified industrial source data. Reference 76.

[h] AP-42 data. References 75 and 77.

[i] Data not necessarily compatible with uncontrolled emissions. Reference 73.

[j] Reference 73.

[k] AP-42 data. Reference 75.

[l] Based on unspecified industrial source data. Reference 48.

[m] AP-42 data. Reference 6.

[n] NA -- Not available.

TABLE 60. FUGITIVE EMISSION FACTORS FOR PRIMARY SLAB ZINC PROCESSING[a]

Emission Factor Rating: E

Process	Uncontrolled emissions[b] (kg/Mg)	Uncontrolled emissions[b] (lb/ton)
Roasting[c]	Negligible	Negligible
Sinter plant[d]		
Windbox	0.12 to 0.55	0.25 to 1.1
Discharge and screens	0.28 to 1.22	0.55 to 2.45
Retort building[e]	1.0 to 2.0	2.0 to 4.0
Casting[f]	1.26	2.52

[a] All emission factors based on quantity of slab zinc produced except as noted.

[b] All data from Reference 60 .

[c] Determined to be negligible.

[d] Based on steel industry operations with emission factors.
Based on quantity of sinter produced.

[e] Based on lead industry operations.

[f] Based on copper industry operations.

The overall uncertainty with regard to size distribution and total particulate emisison rates invalidates the use of either source of data unless verification can be achieved. As mentioned in Section 6.2.2, the lack of sufficient quality data for the determination of total particulate emission factors requires that some data be used. Since the latter source (Ref. 73). reports total particulate emission factors directly, these values will be used, and no particulate size distribution will be included.

Unspecified (Not Included)

A total of two particulate size distribution sampling tests were conducted on both the uncontrolled and ESP controlled emissions from an unspecified sinter plant as reported in the EPA EADS: FPEIS Test Series 3 (Ref. 78). Insufficient data were provided to determine either particulate size distributions or total particulate mass emission factors. The data were reported as particulate loadings at an impactor cutoff diameter without providing the total particulate loading. None of the data were therefore reported.

New Jersey Zinc Co. (Tests 1 to 3)

Total and size-specific particulate emission tests were conducted at three sites at the New Jersey Zinc Co. primary zinc smelter in Palmerton, Pennsylvania (Ref. 73). The tests were conducted at the smelter cokes, vertical retort, and sinter plant. Since this plant is no longer operational, and no other facility exists in the United States which includes a smelter coke, these test data are not reported. Tests on the vertical retort were for uncontrolled stack emissions. Tests on the sinter plant were for both cyclone and cyclone and ESP controlled stack emissions. All tests were conducted using EPA Method 5 stack sampling procedures and an Andersen cascade impactor. Incomplete process data were included, however total and size-specific emission factors were reported directly. The particle sizing was based on a single 2-μm cutpoint, with emission factors reported for particulate matter less than and greater than 2 μm. Since these data are insufficient for the determination of size-specific emission factors, only particulate mass emission factors are reported. The test data were given an A rating.

Unspecified (Various Estimates)

A variety of emission factors were reported in secondary sources. The factors reported were a combination of secondhand test results inadequately referenced for complete verification or explicitly outlined estimates based on assumptions of zinc smelter operations or emission factors developed in similar industries.

The Particulate Pollutant System study was a major source of this type of data. The validity of all of these data is extremely uncertain, and the emission factors developed were given an E rating.

The particulate mass emission factor for fluidized-bed roasting was estimated by assuming an average 70 percent breakthrough of roaster feedstock and a zinc production rate estimated at 60 percent of the roaster feedrate (Ref. 76). This calculates to an uncontrolled fluidized-bed roaster emission factor of 2,000 lb/ton (1,000 kg/Mg) of zinc produced. The particulate mass emission factor for multiple hearth roasting was similarly estimated from an average 10 percent breakthrough of roaster feedstock. This calculates to an uncontrolled multiple hearth roaster emission factor of 333 lb/ton (167 kg/Mg) of zinc produced.

The total emission factor for an uncontrolled sinter plant was reported as 125 lb/ton (62.5 kg/Mg), based on a unspecified industrial source.

The mass emission factors for both a suspension and a fluidized-bed roaster were estimated from data presented in the Encyclopedia of Chemical Technology (Ref. 22). Roaster particulate emissions at one plant were evaluated at 60 percent of roaster feedstock. Using the 60 percent production rate assumption of the previous estimates, results in an emission factor of 2,000 lb/ton (1,167 kg/Mg). Controlled emissions were estimated on the basis of a 99.5 percent efficient cyclone and ESP combination acting on the 80 percent of uncontrolled particulate emissions not dropped out in the waste heat boiler. This results in a controlled emission factor of 8 lb/ton (4 kg/Mg). The uncontrolled fluidized-bed emission factor was estimated from data at an unspecified plant where 70 percent of the calcine left the roaster via the stack. Again the 60 percent production rate assumption was used, resulting in an uncontrolled emission factor of 2,333 lb/ton (1,167 kg/Mg).

The total particulate emission factor for an electric retort furnace was reported as 20 lb/ton (10 kg/Mg) from an unspecified facility (Ref. 73).

Emission factors developed during the previous AP-42 review cycle are presented alongside of the data and estimates developed during the present study. As these values are not the result of actual testing, but are based on engineering judgment and estimates, their validity is suspect.

6.2.2 Data Analysis

Not much data analysis was required in the development of the particulate mass emission factors. In the case of emissions from an uncontrolled sinter plant and a vertical retort, test data replaced what appear to have been estimates in the previous AP-42 section. In the case of suspension roasting, controlled sinter plant operations, electric retorts and the electrolytic process, only single emission factors were located and thus reported directly as found. In the last case, the electrolytic process, the data presented in the previous AP-42 section was not referenced. No data were found to invalidate the value reported, but it is not based on any specific test data or substantiated estimates. Emission factors for multiple hearth and fluidized-bed roasters were averaged from the estimates obtained during the data review. The emission factors developed are presented in Table 61.

Fugitive emission factors were estimated based on comparable facilities in the metals processing industry. The values obtained are reported directly in Table 60.

6.3 CHEMICAL CHARACTERIZATION

The uncontrolled and controlled emissions from a variety of processes within a primary slab zinc processing plant were analyzed for chemical composition. The major component of all particulate emissions was determined to be Zn, with Fe, S, Pb, and Cd as significant minor components.

The chemical composition of two particulate samples obtained from the uncontrolled effluent of a zinc roaster is presented in Table 62. The compositions obtained are fairly consistent with regard to the major constituents (Zn, Fe, S, and Pb), with trace quantities of a range of elements also found.

The particulate emissions from a vertical retort furnace and sinter plant were characterized for trace metal content (Zn, Pb, Cd, and Cu) for particulate less than and greater than 2 μm. The results of this analysis are presented in Table 63. Whereas the chemical composition of vertical retort particulate emissions is basically unaffected by particle size, the cyclone and ESP controlled emissions of a sinter plant is affected by particle size. Twenty-four percent of the particulate emissions less than 2 μm emitted from a sinter plant is zinc, while only 17 percent of particulates greater than 2 μm is zinc.

TABLE 61. TOTAL PARTICULATE EMISSION FACTOR DATA AND ESTIMATES -- PRIMARY SLAB ZINC PROCESSING[a]

Process	Uncontrolled emissions		Emission factor rating	Controlled emissions		Emission factor rating
	(kg/Mg)	(lb/ton)		(kg/Mg)	(lb/ton)	
Roasting						
Multiple hearth	113	227	E	NA	NA[c]	--
Suspension[d]	1,000	2,000	E	4	8	E
Fluidized-bed[e]	1,083	2,167	E	NA	NA	--
Sinter Plant						
Without controls[f]	62.5	125	E	NA	NA	--
With cyclone[g]	--	--	--	24.1	48.2	D
With cyclone and ESP[f]	--	--	--	8.25	16.5	D
Vertical retort[h]	7.15	14.3	D	NA	NA	--
Electric retort[i]	10.0	20.0	E	NA	NA	--
Electrolytic process[j]	3.3	6.6	E	NA	NA	--

[a] All emission factors based on quantity of slab zinc produced.

[b] Averaged from an estimated 10 percent of feed released as particulate emissions and a zinc production role at 60 percent of roaster feedrate (Reference 76), and other estimates (Reference 75.

[c] NA -- not available.

[d] Estimated on the basis of an average 60 percent of feed released as particulate emission and a zinc production rate at 60 percent of roaster feedrate.
Controlled emissions based on 20 percent drop-out in waste heat boiler and 99.5 percent drop-out in cyclone and ESP. References 22 and 76.

[e] Estimated on the basis of an average 65 percent of feed released as particulate emissions and a zinc production rate of 60 percent of roaster feedrate.
Reference 22 and 76 .

[f] Based on unspecified industrial source data. Reference 76 .

[g] Data not necessarily compatible with uncontrolled emissions. Reference 73 .

[h] Reference 73 .

[i] Based on unspecified industrial source data. Reference 48.

[j] Reference 6 .

TABLE 62. PARTICULATE EMISSIONS TRACE METAL CONTENT[a] (PERCENT BY WEIGHT)

Process	Particulate size	Zn	Pb	Cd	Cu
Vertical retort (uncontrolled)	<2 μm	45.2	2.60	0.54	0.008
	>2 μm	43.6	1.80	0.26	0.027
	Total	44.9	2.40	0.46	0.014
Sinter plant (cyclone)	Total	20.3	3.37	8.95	0.062
Sinter plant (cyclone and ESP)	<2 μm	24.2	13.32	19.85	0.042
	>2 μm	17.0	6.22	8.71	0.042
	Total	19.9	9.03	13.12	0.042

[a] All data from Reference 73 .

TABLE 63. PARTICULATE EMISSIONS CHEMICAL COMPOSITION FOR UNCONTROLLED ROASTING EMISSIONS (PERCENT BY WEIGHT)

Process	Zn	Fe	S	Pb	As	Cd	Cu	Mn	Sn	Se	F
Fluid bed[a]	55	8.5	3.0	1.5	tr-13[b]	tr	ND[c]			tr	tr
Multiple hearth, suspension and fluid bed[d]	54	7.0	7.0	1.4		0.41	0.40	0.21	0.01		

[a] Data combined in Reference 42 (from References 79, 80 , and author's calculations).
[b] tr = trace
[c] ND = not detected
[d] Reference 72 .

SECTION 7

PROPOSED AP-42 SECTIONS

The proposed revisions to Sections 7.1, 7.3, 7.6, 7.11 and 7.7 of AP-42 are presented in the following pages as they would appear in the actual document.

AP-42 Section 7.1

Primary Aluminum Production

7.1 PRIMARY ALUMINUM PRODUCTION

7.1.1 Process Description[1-2]

The base ore for primary aluminum production is bauxite, a hydrated oxide of aluminum consisting of 30 to 70 percent alumina (Al_2O_3) and lesser amounts of iron, silicon and titanium. Bauxite ore is purified to alumina by the Bayer process and then is reduced to elemental aluminum. The production of alumina and the reduction of alumina to aluminum are seldom accomplished at the same facility. A schematic diagram of the primary production of aluminum is shown at Figure 7.1-1.

In the Bayer process, the ore is dried, ground in ball mills and mixed with a leaching solution of sodium hydroxide at an elevated temperature and pressure, producing a sodium aluminate solution which is separated from the bauxite impurities and cooled. As the solution cools, hydrated aluminum oxide ($Al_2O_3 \cdot 3H_2O$) precipitates. After separation and washing to remove sodium hydroxide and other impurities, the hydrated aluminum oxide is dried and is calcined to produce a crystalline form of alumina, advantageous for electrolysis.

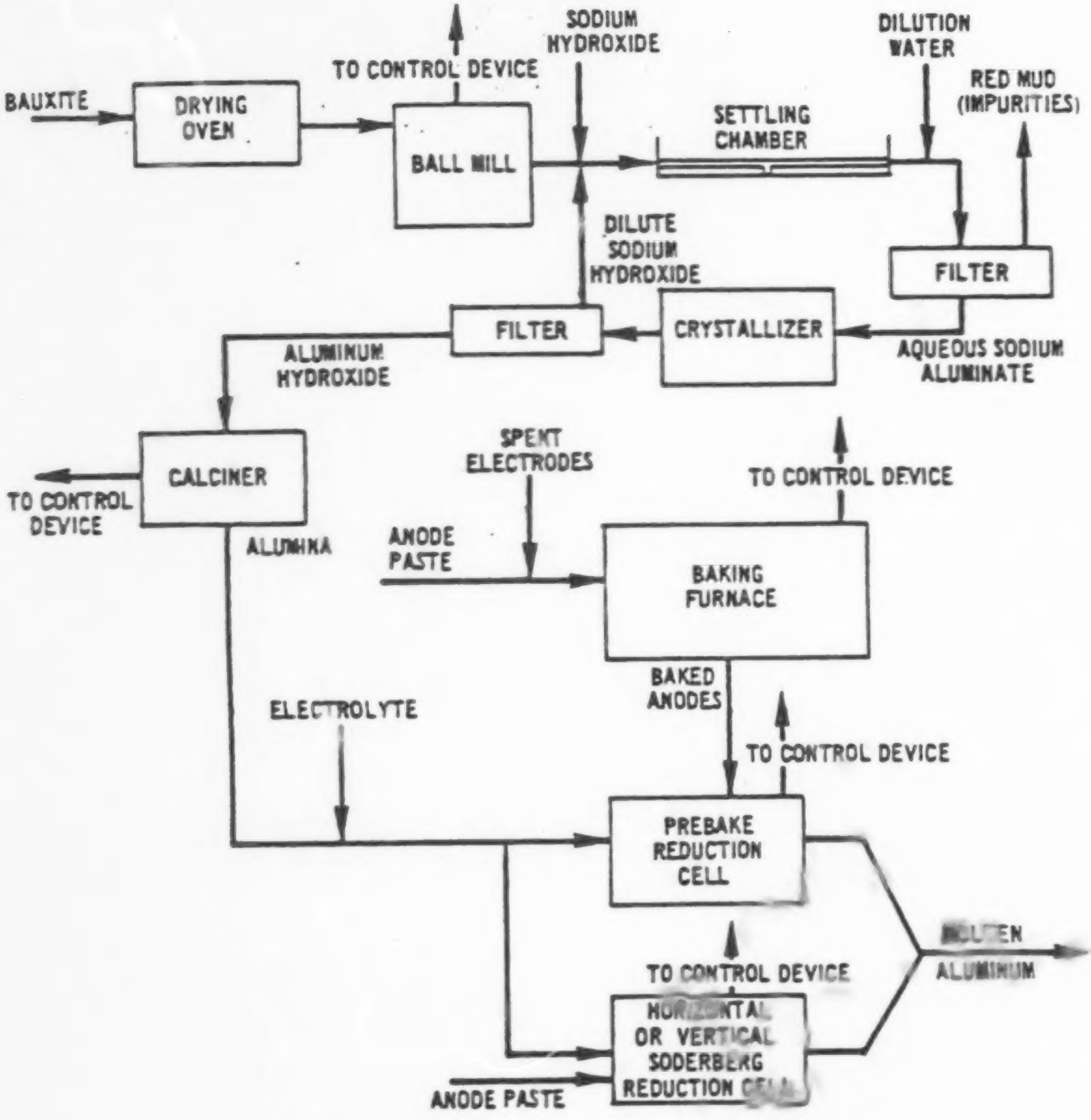
To produce aluminum metal, the crystalline Al_2O_3 is put through the Hall-Heroult process, an electrolytic reduction of alumina dissolved in a molten salt bath of cryolite (Na_3AlF_6) and various salt additives:

$$\underset{\text{(Alumina)}}{2Al_2O_3} \quad \underset{\text{(Reduction)}}{\xrightarrow{\text{Electrolysis}}} \quad \underset{\text{(Aluminum)}}{4Al} + \underset{\text{(Oxygen)}}{3O_2}$$

The electrolytic reduction occurs in shallow rectangular cells, or "pots", which which are steel shells lined with carbon. Carbon electrodes extending into the pot serve as the anodes and the carbon lining the steel shell is the cathode. Molten cryolite functions as both the electrolyte and the solvent for the alumina. Electrical resistance to the current passing between the electrodes generates heat that maintains cell operating temperatures between 950° and 1000°C (1730° and 1830°F). Aluminum is deposited at the cathode, where it remains as molten metal below the surface of the cryolite bath. The carbon anodes are continuously depleted by the reaction of oxygen (formed during the reaction) and anode carbon, producing carbon monoxide and carbon dioxide. Carbon consumption and other raw material and energy requirements for aluminum production are summarized in Table 7.1-1. The aluminum product is periodically tapped beneath the cryolite cover and fluxed to remove trace impurities.

Three types of aluminum reduction cells are now in use, distinguished by anode type and pot configuration: prebaked (PB), horizontal stud Soderberg (HSS), and vertical stud Soderberg (VSS).

Most of the aluminum produced in the U. S. is processed in PB cells. Anodes are produced as an ancillary operation at a reduction plant. In a paste preparation plant, petroleum coke is mixed with a pitch binder to form a paste which is used both for Soderberg cell anodes and for green anodes used in



SODIUM HYDROXIDE
DILUTION WATER
TO CONTROL DEVICE
RED MUD (IMPURITIES)
BAUXITE
DRYING OVEN
BALL MILL
SETTLING CHAMBER
DILUTE SODIUM HYDROXIDE
FILTER
FILTER
CRYSTALLIZER
ALUMINUM HYDROXIDE
AQUEOUS SODIUM ALUMINATE
SPENT ELECTRODES
TO CONTROL DEVICE
CALCINER
TO CONTROL DEVICE
ALUMINA
ANODE PASTE
BAKING FURNACE
BAKED ANODES
ELECTROLYTE
TO CONTROL DEVICE
PREBAKE REDUCTION CELL
MOLTEN ALUMINUM
TO CONTROL DEVICE
HORIZONTAL OR VERTICAL SODERBERG REDUCTION CELL
ANODE PASTE

Figure 7.1-1. Schematic diagram of aluminum production process.

prebake cells. Paste preparation includes crushing, grinding and screening of coke and cleaned spent anodes (butts), and blending with a pitch binder in a steam jacketed mixer. For Soderberg anodes, the thick paste mixture is transferred directly to the pot room and added to the anode casings. In prebake anode preparation, the paste mixture is molded to form self supporting green anode blocks. These blocks are baked in a direct fired ring furnace or an indirect fired tunnel kiln. Baked anodes are then transferred to the rodding room for attachment of electrical connections. Volatile organic vapors from the pitch paste are emitted during anode baking, most of which are destroyed in the baking furnace. The baked anodes, typically 14 to 24 per cell, are attached to metal rods and are expended as they are used.

In the electrolytic reduction of alumina, the carbon anodes are lowered into the cell and are consumed at a rate of about 2.5 centimeters (1 inch) per day. PB cells are preferred over Soderberg cells for their lower power requirements, reduced generation of volatile pitch vapors from the carbon anodes, and provision for better cell hooding to capture emissions.

The next most common reduction cell is the horizontal stud Soderberg. This type of cell uses a "continuous" carbon anode. Green anode paste is periodically added at the top of the anode casing of the pot and is baked by the heat of the cell into a solid carbon mass, as the material moves down the casing. The cell casing is of aluminum or steel sheeting, permanent steel skirt and perforated steel channels, through which electrode connections (studs) are inserted horizontally into the anode paste. During reduction, as the baking anode is lowered, the lower row of studs and the bottom channel are removed, and the flexible electrical connectors are moved to a higher row of studs.

TABLE 7.1-1. RAW MATERIAL AND ENERGY REQUIREMENTS FOR ALUMINUM PRODUCTION

Parameter	Typical value
Cell operating temperature	950°C (1740°F)
Current through pot line	60,000 to 280,000 amperes
Voltage drop per cell	4.0 to 5.2
Current efficiency	85 to 95 %
Energy required	13.2 to 18.7 kwh/kg (6.0 to 8.5 kwh/lb) aluminum
Weight alumina consumed	1.89 to 1.92 kg (lb) Al_2O_3/ kg (lb) aluminum
Weight electrolyte fluoride consumed	0.03 to 0.10 kg (lb) fluoride/
Weight carbon electrode consumed	0.45 to 0.55 kg (lb) electrode/ kg (lb) aluminum

High molecular weight organics from the anode paste are released, along with other emissions. The heavy tars can cause plugging of exhaust ducts, fans and emission control equipment.

The vertical stud Soderberg cell is similar to the HSS cell, except that the studs are mounted vertically in the anode paste. Gases from the VSS cells can be ducted to gas burners, and the tars and oils combusted. VSS cell construction prevents the installation of an integral gas collection device, and hooding is restricted to a canopy or skirt at the base of the cell where the hot anode enters the cell bath.

Casting involves pouring molten aluminum into molds and cooling it with water. At some plants before casting, the molten aluminum may be batch treated in furnaces to remove oxide, gaseous impurities and active metals such as sodium and magnesium. One process consists of adding a flux of chloride and fluoride salts and then bubbling chlorine gas, usually mixed with an inert gas, through the molten mixture. Chlorine reacts with the impurities to form HCl, Al_2O_3 and metal chloride emissions. A dross forms to float on the molten aluminum and is removed before casting.[12]

7.1.2 Emissions And Controls[1-8,11]

Controlled and uncontrolled emission factors for total particulate matter, fluoride and sulfur oxides are in Table 7.1-2. Fugitive particulate and fluoride emission factors for reduction cells are also presented in this Table. Tables 7.1-3 through 7.1-5 and Figures 7.1-2 through 7.1-4 give size specific particulate matter emissions for primary aluminum industry processes for which this information is available.

Large amounts of particulate are generated during the calcining of hydrated aluminum oxide, but the economic value of this dust is such that extensive controls are used to reduce emissions to relatively small quantities. Small amounts of particulate are emitted from the bauxite grinding and materials handling processes.

Emissions from aluminum reduction processes are primarily gaseous hydrogen fluoride and particulate fluorides, alumina, carbon monoxide, volatile organics, and sulfur dioxide from the reduction cells; and fluorides, vaporized organics and sulfur dioxide from the anode baking furnaces.

The source of fluoride emissions from reduction cells is the fluoride electrolyte, which contains cryolite, aluminum fluoride (AlF_3) and fluorspar (CaF_2). For normal operation, the weight, or "bath", ratio of sodium fluoride (NaF) to AlF_3 is kept between 1.36 and 1.43 by the addition of AlF3. This increases the cell current efficiency and lowers the bath melting point permitting lower operating temperatures in the cell. All fluoride emissions are also decreased by lowering the operating temperature. The ratio of gaseous (mainly hydrogen fluoride and silicon tetrafluoride) to particulate fluorides varies from 1.2 to 1.7 with PB and HSS cells, but attains a value of approximately 3.0 with VSS cells.

Particulate emissions from reduction cells are alumina and carbon from anode dusting, cryolite, aluminum fluoride, calcium fluoride, chiolite

TABLE 7.1-2. EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION PROCESSES[a,b]

EMISSION FACTOR RATING: A

Operation	Total particulate[c]		Gaseous fluoride		Particulate fluoride		Reference
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	
Bauxite grinding							
Uncontrolled	3.0	6.0	Neg		NA		1,3
Spray tower	0.9	1.8	Neg		NA		1,3
Floating bed scrubber	0.85	1.7	Neg		NA		1,3
Quench tower and spray screen	0.5	1.0	Neg		NA		1,3
Aluminum hydroxide calcining							
Uncontrolled[d]	100.0	200.0	Neg		NA		1,3
Spray tower	30.0	60.0	Neg		NA		1,3
Floating bed scrubber	28.0	56.0	Neg		NA		1,3
Quench tower	17.0	34.0	Neg		NA		1,3
ESP	2.0	4.0	Neg		NA		1,3
Anode baking furnace							
Uncontrolled	1.5	3.0	0.45	0.9	0.05	0.1	2,10-11
Fugitive	NA	NA	NA	NA	NA	NA	
Spray tower	0.375	0.75	0.02	0.04	0.015	0.03	10
ESP	0.375	0.75	0.02	0.04	0.015	0.03	2
Dry alumina scrubber	0.03	0.06	0.0045	0.009	0.001	0.002	2,10
Prebake cell							
Uncontrolled	47.0	94.0	12.0	24.0	10.0	20.0	1-2,10-11
Fugitive	2.5	5.0	0.6	1.2	0.5	1.0	2,10
Emissions to collector	44.5	89.0	11.4	22.8	9.5	19.0	2
Multiple cyclones	9.8	19.6	11.4	22.8	2.1	4.2	2
Dry alumina scrubber	0.9	1.8	0.1	0.2	0.2	0.4	2,10
Dry ESP plus spray tower	2.25	4.5	0.7	1.4	1.7	3.4	2,10
Spray tower	8.9	17.8	0.7	1.4	1.9	3.8	2
Floating bed scrubber	8.9	17.8	0.25	0.5	1.9	3.8	2
Coated bag filter dry scrubber	0.9	1.8	1.7	3.4	0.2	0.4	2
Cross flow packed bed	13.15	26.3	3.25	6.7	2.8	5.6	10
Dry plus secondary scrubber	0.35	0.7	0.2	0.4	0.15	0.3	10
Vertical Soderberg stud cell							
Uncontrolled	39.0	78.0	16.5	33.0	5.5	11.0	2,10
Fugitive	6.0	12.0	2.45	4.9	0.85	1.7	10
Emissions to collector	33.0	66.0	14.05	28.1	4.65	9.3	10
Spray tower	8.25	16.5	0.15	0.3	1.15	2.3	2
Venturi scrubber	1.3	2.6	0.15	0.3	0.2	0.4	2
Multiple cyclones	16.5	33.0	14.05	28.1	2.35	4.7	2
Dry alumina scrubber	0.65	1.3	0.15	0.3	0.1	0.2	2
Scrubber plus ESP plus spray screen and scrubber	3.85	7.7	0.75	1.5	0.65	1.3	2
Horizontal Soderberg stud cell							
Uncontrolled	49.0	98.0	11.0	22.0	6.0	12.0	2,10
Fugitive	5.0	10.0	1.1	2.2	0.6	1.2	2,10
Emissions to collector	44.0	88.0	9.9	19.8	5.4	10.8	2,10
Spray tower	11.0	22.0	3.75	7.5	1.35	2.7	2,10
Floating bed scrubber	9.7	19.4	0.2	0.4	1.2	2.4	2
Scrubber plus wet ESP	0.9	1.8	0.1	0.2	0.1	0.2	2,10
Wet ESP	0.9	1.8	0.5	1.0	0.1	0.2	10
Dry alumina scrubber	0.9	1.8	0.2	0.4	0.1	0.2	10

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[a] For bauxite grinding, expressed as kg/Mg (lb/ton) of bauxite processed. For aluminum hydroxide calcining, expressed as kg/Mg (lb/ton) of alumina produced. All other factors are/Mg (ton) of molten aluminum product. ESP= electrostatic precipitator. NA = not available. Neg = negligible.

[b] Sulfur oxides may be estimated, with an Emission Factor Rating of C, by the following calculations.

Anode baking furnace, uncontrolled SO_2 emissions (excluding furnace fuel combustion emissions):

$$20(C)(S)(1-0.01\ K)\ \text{kg/Mg}\ [40(C)(S)(1-0.01\ K)\ \text{lb/ton}]$$

Prebake (reduction) cell, uncontrolled SO_2 emissions:

$$0.2(C)(S)(K)\ \text{kg/Mg}\ [0.4(C)(S)(K)\ \text{lb/ton}]$$

Where: C = Anode consumption* during electrolysis, lb anode consumed/lb Al produced
S = % sulfur in anode before baking
K = % of total SO_2 emitted by prebake (reduction) cells.

*Anode consumption weight is weight of anode paste (coke + pitch) before baking.

[c] Includes particulate fluorides.

[d] After multicyclone.

TABLE 7.1-3. UNCONTROLLED EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR ROOF MONITOR FUGITIVE EMISSIONS FROM PREBAKE ALUMINUM CELLS[a]

EMISSION FACTOR RATING: C

Particle size[b] (um)	Cumulative mass % ≤stated size	Cumulative emission factor	
		kg/Mg Al	lb/ton Al
15	65	1.62	3.23
10	58	1.45	2.90
5	43	1.08	2.15
2.5	28	0.70	1.40
1.25	18	0.46	0.92
0.625	13	0.33	0.67
Total	100	2.5	5.0

[a] Reference 4.

[b] Expressed as equivalent aerodynamic particle diameter.

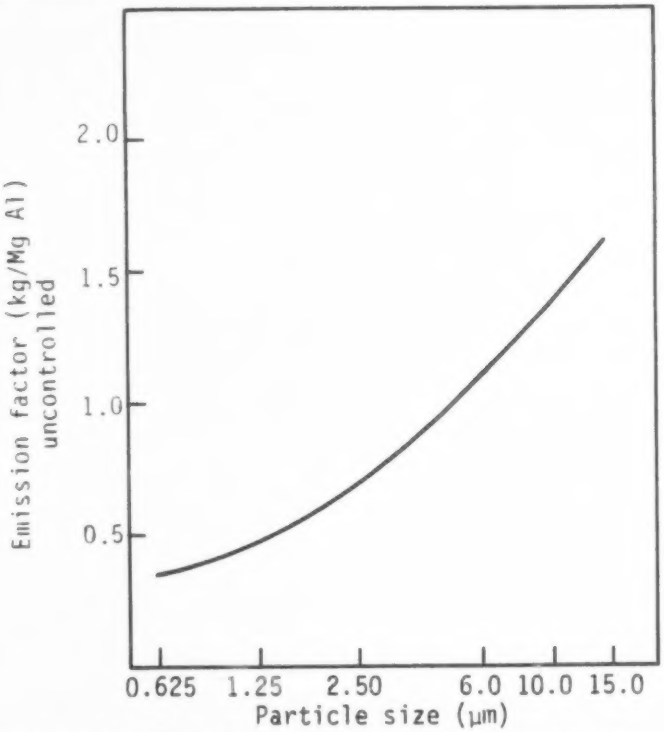

Figure 7.1-2. Emission factors less than stated particle size for fugitive emissions from prebake aluminum cells.

TABLE 7.1-4. UNCONTROLLED EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR ROOF MONITOR FUGITIVE EMISSIONS FROM HSS ALUMINUM CELLS[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤stated size	Cumulative emission factors	
		kg/Mg Al	lb/ton Al
15	39	1.95	3.9
10	31	1.55	3.1
5	23	1.15	2.3
2.5	17	0.85	1.7
1.25	13	0.65	1.3
0.625	8	0.40	0.8
Total	100	5.0	10.0

[a] Reference 4.

[b] Expressed as equivalent aerodynamic particle diameter.

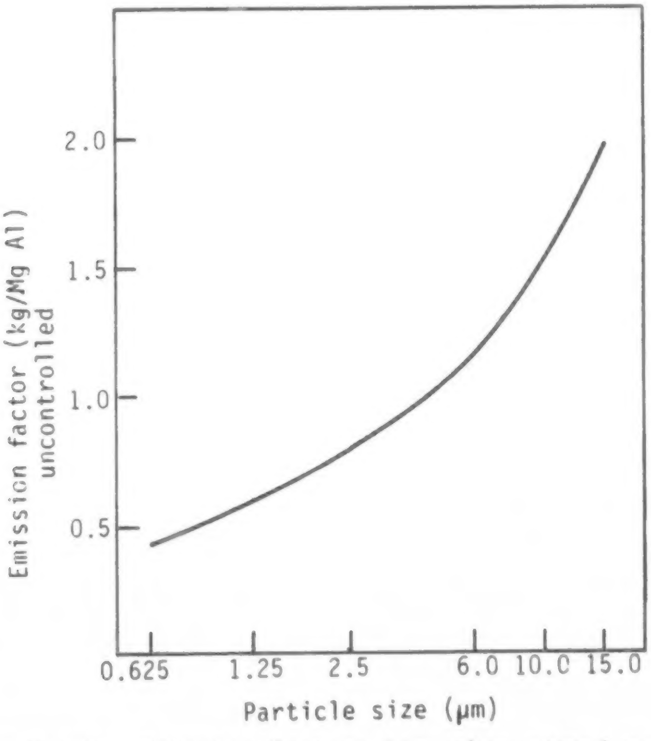

Figure 7.1-3. Emission factors less than stated particle size for fugitive emissions from HSS aluminum cells.

TABLE 7.1-5. UNCONTROLLED EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR PRIMARY EMISSIONS FROM HSS REDUCTION CELLS[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤stated size	Cumulative emission factors	
		kg/Mg Al	lb/ton Al
15	63	30.9	61.7
10	58	28.4	56.8
5	50	24.5	49.0
2.5	40	19.6	39.2
1.25	32	15.7	31.4
0.625	26	12.7	25.5
Total	100	49.0	98.0

[a] Reference 4.

[b] Expressed as equivalent aerodynamic particle diameter.

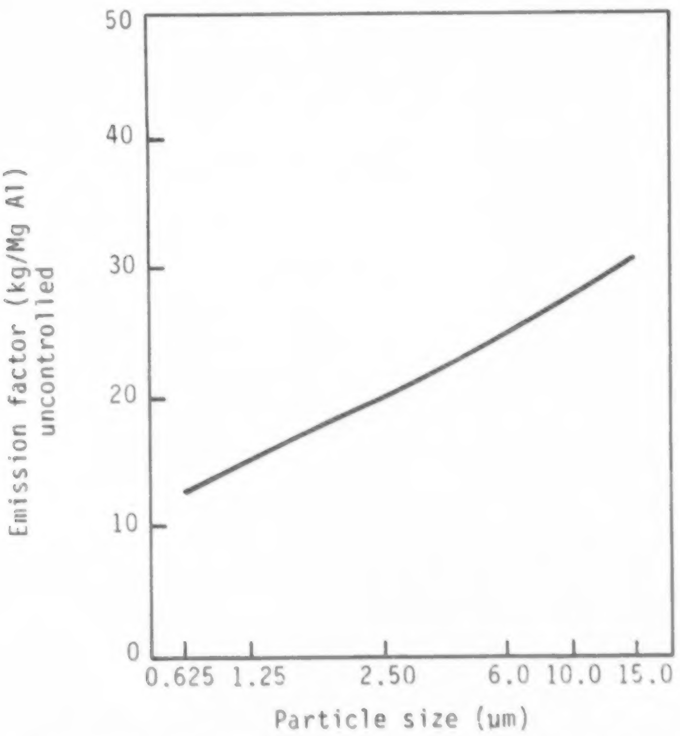

Figure 7.1-4. Cumulative emission factors less than stated particle size for primary emissions from HSS reduction cells.

($Na_5Al_3F_{14}$) and ferric oxide. Representative size distributions for fugitive emissions from PB and HSS plants and for particulate emissions from HSS cells are presented in Tables 7.1-3 through 7.1-5.

Emissions from reduction cells also include hydrocarbons or organics, carbon monoxide and sulfur oxides. Small amounts of hydrocarbons are released by PB pots, and larger amounts are emitted from HSS and VSS pots. In vertical cells, these organics are incinerated in integral gas burners. Sulfur oxides originate from sulfur in the anode coke and pitch, and concentrations of sulfur oxides in VSS cell emissions range from 200 to 300 parts per million. Emissions from PB plants usually have SO_2 concentrations ranging from 20 to 30 parts per million.

Emissions from anode bake ovens include the products of fuel combustion; high boiling organics from the cracking, distillation, and oxidation of paste binder pitch; sulfur dioxide from the sulfur in carbon paste, primarily from the petroleum coke; fluorides from recycled anode butts; and other particulate matter. Concentrations of uncontrolled S02 emissions from anode baking furnaces range from 5 to 47 parts per million (based on 3 percent sulfur in coke).[9]

A variety of control devices has been used to abate emissions from reduction cells and anode baking furnaces. To control gaseous and particulate fluorides and particulate emissions, one or more types of wet scrubbers (spray tower and chambers, quench towers, floating beds, packed beds, venturis) have been applied to all three types of reduction cells and to anode baking furnaces. Also, particulate control methods such as wet and dry electrostatic precipitators, multiple cyclones and dry alumina scrubbers (fluid bed, injected, and coated filter types) are used with baking furnaces and on all three cell types. Also, the alumina adsorption systems are being used on all three cell types to control both gaseous and particulate fluorides by passing the pot offgases through the entering alumina feed, which adsorbs the fluorides. This technique has an overall control efficiency of 98 to 99 percent. Baghouses are then used to collect residual fluorides entrained in the alumina and recycle them to the reduction cells. Wet ESPs approach adsorption in particulate removal efficiency, but they must be coupled to a wet scrubber or coated baghouse to catch hydrogen fluoride.

Scrubber systems also remove a portion of the SO_2 emissions. These emissions could be reduced by wet scrubbing or by reducing the quantity of sulfur in the anode coke and pitch, i. e., calcining the coke.

In hydrated aluminum oxide calcining, bauxite grinding, and materials handling operations, various dry dust collection devices (centrifugal collectors, multiple cyclones, or ESPs and/or wet scrubbers) have been used.

Potential sources of fugitive particulate emissions in the primary aluminum industry are bauxite grinding, materials handling, anode baking, and three types of reduction cells (see Table 7.1-2). These fugitives probably have particulate size distributions similar to those presented in Table 7.1-3.

References for Section 7.1

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5. Emissions from Wet Scrubbing System, Y-7730-E, York Research Corporation, Stamford, CT, May 1972.

6. Emissions From Primary Aluminum Smelting Plant, Y-7730-B, York Research Corporation, Stamford, CT, June 1972.

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AP-42 Section 7.3

Primary Copper Smelting

7.3 PRIMARY COPPER SMELTING

7.3.1 Process Description[1-3]

In the United States, copper is produced from sulfide ore concentrates, principally by pyrometallurgical smelting methods. Because the ores usually contain less than 1 percent copper, they must be concentrated before transport to smelters. Concentrations of 15 to 35 percent copper are accomplished at the mine site by crushing, grinding and flotation. Sulfur content of the concentrate ranges from 25 to 35, percent and most of the remainder is iron (25 percent) and water (10 percent). Some concentrates also contain significant quantities of arsenic, cadmium, lead, antimony, and other heavy metals.

A conventional pyrometallurgical copper smelting process is illustrated in Figure 7.3-1. The process includes roasting of ore concentrates to produce calcine, smelting of roasted (calcine feed) or unroasted (green feed) ore concentrates to produce matte, and converting of the matte to yield blister copper product (about 99 percent pure). Typically, the blister copper is fire refined in an anode furnace, cast into "anodes" and sent to an electrolytic refinery for further impurity elimination.

In roasting, charge material of copper concentrate mixed with a siliceous flux (often a low grade ore) is heated in air to about 650°C (1200°F), eliminating 20 to 50 percent of the sulfur as sulfur dioxide (SO_2). Portions of such impurities as antimony, arsenic and lead are driven off, and some iron is converted to oxide. The roasted product, calcine, serves as a dried and heated charge for the smelting furnace. Either multiple hearth or fluidized bed roasters are used for roasting copper concentrate. Multiple hearth roasters accept moist concentrate, whereas fluid bed roasters are fed finely ground material (60 percent minus 200 mesh). With both of these types, the roasting is autogenous. Because there is less air dilution, higher SO_2 concentrations are present in fluidized bed roaster gases than in multiple hearth roaster gases.

In the smelting process, either hot calcines from the roaster or raw unroasted concentrate is melted with siliceous flux in a smelting furnace to produce copper matte, a molten mixture of cuprous sulfide (Cu_2S), ferrous sulfide (FeS) and some heavy metals. The required heat comes from partial oxidation of the sulfide charge and from burning external fuel. Most of the iron and some of the impurities in the charge oxidize with the fluxes to form atop the molten bath a slag, which is periodically removed and discarded. Copper matte remains in the furnace until tapped. Mattes produced by the domestic industry range from 35 to 65 percent copper, with 45 percent the most common. The copper content percentage is referred to as the matte grade. Currently, five smelting furnace technologies are used in the U. S., reverberatory, electric, Noranda, Outokumpu (flash), and Inco (flash).

Reverberatory furnace operation is a continuous process, with frequent charging of input materials and periodic tapping of matte and skimming of slag.

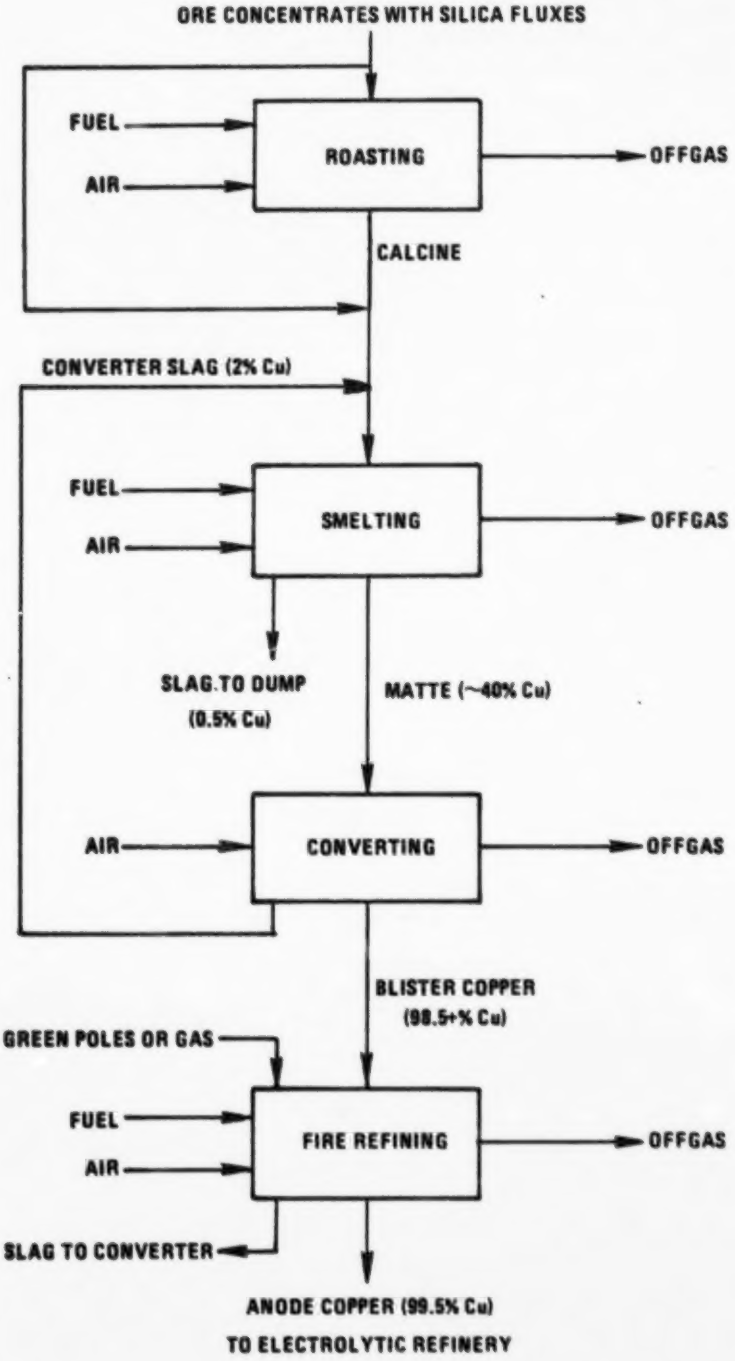
ORE CONCENTRATES WITH SILICA FLUXES
FUEL
AIR
ROASTING
OFFGAS
CALCINE
CONVERTER SLAG (2% Cu)
FUEL
AIR
SMELTING
OFFGAS
SLAG TO DUMP
(0.5% Cu)
MATTE (~40% Cu)
AIR
CONVERTING
OFFGAS
BLISTER COPPER
(98.5+% Cu)
GREEN POLES OR GAS
FUEL
AIR
FIRE REFINING
OFFGAS
SLAG TO CONVERTER
ANODE COPPER (99.5% Cu)
TO ELECTROLYTIC REFINERY

Figure 7.3-1. Typical primary copper smelter process.

1300 tons) of charge per day. Heat is supplied by combustion of oil, gas or pulverized coal, and furnace temperature may exceed 1500°C (2730°F).

For smelting in electric arc furnaces, heat is generated by the flow of an electric current in carbon electrodes lowered through the furnace roof and submerged in the slag layer of the molten bath. The feed generally consists of dried concentrates or calcines, and charging wet concentrates is avoided. The chemical and physical changes occurring in the molten bath are similar to those occurring in the molten bath of a reverberatory furnace. Also, the matte and slag tapping practices are similar at both furnaces. Electric furnaces do not produce fuel combustion gases, so flow rates are lower and SO_2 concentrations higher in the effluent gas than in that of reverberatory furnaces.

Flash furnace smelting combines the operations of roasting and smelting to produce a high grade copper matte from concentrates and flux. In flash smelting, dried ore concentrates and finely ground fluxes are injected, together with oxygen, preheated air, or a mixture of both, into a furnace of special design, where temperature is maintained at approximately 1000°C (1830°F). Flash furnaces, in contrast to reverberatory and electric furnaces, use the heat generated from partial oxidation of their sulfide charge to provide much or all of the energy (heat) required for smelting. They also produce offgas streams containing high concentrations of SO_2.

Slag produced by flash furnace operations contains significantly higher amounts of copper than does that from reverberatory or electric furnace operations. As a result, the flash furnace and converter slags are treated in a slag cleaning furnace to recover the copper. Slag cleaning furnaces usually are small electric furnaces. The flash furnace and converter slags are charged to a slag cleaning furnace and are allowed to settle under reducing conditions, with the addition of coke or iron sulfide. The copper, which is in oxide form in the slag, is converted to copper sulfide, is subsequently removed from the furnace and is charged to a converter with regular matte. If the slag's copper content is low, the slag is discarded.

The Noranda process, as originally designed, allowed the continuous production of blister copper in a single vessel by effectively combining roasting, smelting and converting into one operation. Metallurgical problems, however, led to the operation of these reactors for the production of copper matte. As in flash smelting, the Noranda process takes advantage of the heat energy available from the copper ore. The remaining thermal energy required is supplied by oil burners, or by coal mixed with the ore concentrates.

The final step in the production of blister copper is converting, with the purposes of eliminating the remaining iron and sulfur present in the matte and leaving molten "blister" copper. All but one U. S. smelter uses Pierce-Smith converters, which are refractory lined cylindrical steel shells mounted on trunnions at either end, and rotated about the major axis for charging and pouring. An opening in the center of the converter functions as a mouth through which molten matte, siliceous flux, and scrap copper are charged and gaseous products are vented. Air or oxygen rich air is blown through the molten matte. Iron sulfide (FeS) is oxidized to iron oxide (FeO) and SO_2, and the FeO blowing and slag skimming are repeated until an adequate amount of relatively pure Cu_2S, called "white metal", accumulates in the bottom of the converter. A renewed air blast oxidizes the copper sulfide sulfur to SO_2, leaving blister copper in the converter. The blister copper is subsequently removed and transferred to refining facilities. This segment of converter operation is termed the finish blow. The SO_2 produced throughout the operation is vented to pollution control devices.

One domestic smelter uses Hoboken converters, the primary advantage of which lies in emission control. The Hoboken converter is essentially like a conventional Pierce-Smith converter, except that this vessel is fitted with a side flue at one end shaped as an inverted U. This flue arrangement permits siphoning of gases from the interior of the converter directly to the offgas collection system, leaving the converter mouth under a slight vacuum.

Blister copper usually contains from 98.5 to 99.5 percent pure copper. Impurities may include gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulfur, tellurium, and zinc. To purify blister copper further, fire refining and electrolytic refining are used. In fire refining, blister copper is placed in a fire refining furnace, a flux is usually added, and air is blown through the molten mixture to oxidize remaining impurities, which are removed as a slag. The remaining metal bath is subjected to a reducing atmosphere to reconvert cuprous oxide to copper. Temperature in the furnace is around 1100°C (2010°F). The fire refined copper is cast into anodes, after which, further electrolytic refining separates copper from impurities by electrolysis in a solution containing copper sulfate and sulfuric acid. Metallic impurities precipitate from the solution and form a sludge that is removed and treated to recover precious metals. Copper is dissolved from the anode and deposited at the cathode. Cathode copper is remelted and made into bars, ingots or slabs for marketing purpose. The copper produced is 99.95 to 99.97 percent pure.

7.3.2 Emissions And Controls

Particulate matter and sulfur dioxide are the principal air contaminants emitted by primary copper smelters. These emissions are generated directly from the processes involved, as in the liberation of SO_2 from copper concentrate during roasting, or in the volatilization of trace elements as oxide fumes. Fugitive emissions are generated by leaks from major equipment during material handling operations.

Roasters, smelting furnaces and converters are sources of both particulate matter and sulfur oxides. Copper and iron oxides are the primary constituents of the particulate matter, but other oxides, such as arsenic, antimony, cadmium, lead, mercury and zinc, may also be present, with metallic sulfates and sulfuric acid mist. Fuel combustion products also contribute to the particulate emissions from multiple hearth roasters and reverberatory furnaces.

Single stage electrostatic precipitators (ESP) are widely used in the primary copper industry to control particulate emissions from roasters, smelting furnaces and converters. Many of the existing ESPs are operated at elevated temperatures, usually from 200° to 340°C (400° to 650°F) and are termed "hot ESPs". If properly designed and operated, these ESPs remove 99 percent or more of the condensed particulate matter present in gaseous effluents. However, at these elevated temperatures, a significant amount of volatile emissions such as arsenic trioxide (As_2O_3) and sulfuric acid mist is present as vapor in the gaseous effluent and thus can not be collected by the particulate control device at elevated temperatures. At these temperatures, the arsenic trioxide in the vapor state will pass through an ESP. Therefore, the gas stream to be treated must be cooled sufficiently to assure that most of the arsenic present is condensed before entering the control device for collection. At some smelters, the gas effluents are cooled to about 120°C (250°F) temperature before entering a particulate control system, usually an ordinary ("cold") ESP. Spray chambers or air infiltration are used for gas cooling. Fabric filters can also be used for particulate matter collection.

Gas effluents from roasters usually are sent to an ESP or spray chamber/ESP system or are combined with smelter furnace gas effluents before particulate collection. Overall, the hot ESPs remove only 20 to 80 percent of the total particulate (condensed and vapor) present in the gas. Cold ESPs may remove more than 95 percent of the total particulate present in the gas. Particulate collection systems for smelting furnaces are similar to those for roasters. Reverberatory furnace offgases are usually routed through waste heat boilers and low velocity balloon flues to recover large particles and heat, then are routed through an ESP or spray chamber/ESP system.

In the standard Pierce-Smith converter, flue gases are captured during the blowing phase by the primary hood over the converter mouth. To prevent the hood's binding to the converter with splashing molten metal, there is a gap between the hood and the vessel. During charging and pouring operations, significant fugitives may be emitted when the hood is removed to allow crane access. Converter offgases are treated in ESPs to remove particulate matter and in sulfuric acid plants to remove SO_2.

Remaining smelter processes handle material that contains very little sulfur, hence SO_2 emissions from these processes are relatively insignificant. Particulate emissions from fire refining operations, however, may be of concern. Electrolytic refining does not produce emissions unless the associated sulfuric acid tanks are open to the atmosphere. Crushing and grinding systems used in ore, flux and slag processing also contribute to fugitive dust problems.

Control of SO_2 emissions from smelter sources is most commonly performed in a single or double contact sulfuric acid plant. Use of a sulfuric acid plant to treat copper smelter effluent gas streams requires that gas be free from particulate matter and that a certain minimum SO_2 concentration be maintained. Practical limitations have usually restricted sulfuric acid plant application to gas streams that contain at least 3 percent SO_2. Table 7.3-1 shows typical average SO_2 concentrations for the various smelter unit offgases. Currently, converter gas effluents at most smelters are treated for SO_2 control in sulfuric acid plants. Gas effluents of some multiple hearth roaster operations and of all fluid bed roaster operations also are treated in sulfuric acid plants. The weak SO_2 content gas effluents from reverberatory furnace operations are usually released to the atmosphere with no reduction of SO_2. The gas effluents from the other types of smelter furnaces, because of their higher contents of SO_2, are treated in sulfuric acid plants before being vented. Typically, single contact acid plants achieve 92.5 to 98 percent conversion of SO_2 to acid, with approximately 2000 parts per million SO_2 remaining in the acid plant effluent gas. Double contact acid plants collect from 98 to more than 99 percent of the SO_2 and emit about 500 parts per million SO_2. Absorption of the SO_2 in dimethylaniline (DMA) solution has also been used in U. S. smelters to produce liquid SO_2.

TABLE 7.3-1. TYPICAL SULFUR DIOXIDE CONCENTRATIONS IN OFFGASES FROM PRIMARY COPPER SMELTING SOURCES

Unit	SO_2 concentration (volume %)
Multiple hearth roaster	1.5 to 3
Fluidized bed roaster	10 to 12
Reverberatory furnace	0.5 to 1.5
Electric arc furnace	4 to 8
Flash smelting furnace	10 to 70
Continuous smelting furnace	5 to 15
Pierce-Smith converter	4 to 7
Hoboken converter	8
Single contact H_2SO_4 plant	0.2 to 0.26
Double contact H_2SO_4 plant	0.05

Emissions from hydrometallurgical smelting plants generally are small in quantity and are easily controlled. In the Arbiter process, ammonia gas escapes from the leach reactors, mixer/settlers, thickeners and tanks. For control, all of these units are covered and are vented to a packed tower scrubber to recover and recycle the ammonia.

Actual emissions from a particular smelter unit depend upon the configuration of equipment in that smelting plant and its operating parameters. Table 7.3-2 gives the emission factors for various smelter configurations, and Tables 7.3-3 through 7.3-5 and Figures 7.3-2 through 7.3-4 give size specific emission factors for those copper production processes, where information is available.

7.3.3 Fugitive Emissions

The process sources of particulate matter and SO_2 emission are also the potential fugitive sources of these emissions: roasting, smelting, converting, fire refining and slag cleaning. Table 7.3-6 presents the potential fugitive emission factors for these sources, while Tables 7.3-7 through 7.3-9 and Figures 7.3-5 through 7.3-7 present cumulative size specific particulate emission factors for fugitive emissions from reverberatory furnace matte, slag tapping, converter slag, and copper blow operations. The actual quantities of emissions from these sources depend on the type and condition of the equipment and on the smelter operating techniques. Although emissions from many of these sources are released inside a building, ultimately they are discharged to the atmosphere.

TABLE 7.3-2. EMISSION FACTORS FOR PRIMARY COPPER SMELTERS[a,b]

EMISSION FACTOR RATING: B

Configuration[c]	By unit	Particulate		Sulfur dioxide[d]		References
		kg/Mg	lb/ton	kg/Mg	lb/ton	
Reverberatory furnace (RF)	RF	25	50	160	320	4-10,
followed by converters (C)	C	18	36	370	740	9,11-15
Multiple hearth roaster (MHR)	MHR	22	45	140	280	4-5,16-17
followed by reverberatory	RF	25	50	90	180	4-9,18-19
furnace (RF) and converters (C)	C	18	36	300	600	8,11-13
Fluid bed roaster (FBR) followed	FBR	NA	NA	180	360	20
by reverberatory furnace (RF)	RF	25	50	90	160	e
and converters (C)	C	18	36	270	540	e
Concentrate dryer (CD) followed	CD	5	10	0.5	1	21-22
by electric furnace (EF) and	EF	50	100	120	240	15
converters (C)	C	18	36	410	820	8,11-13,15
Fluid bed roaster (FBR) followed	FBR	NA	NA	180	360	20
by electric furnace (EF) and	EF	50	100	45	90	15,23
converters (C)	C	18	36	300	600	e
Concentrate dryer (DC) followed	CD	5	10	0.5	1	21-22
by flash furnace (FF),	FF	70	140	410	820	24
cleaning furnace (SS) and	SS[f]	5	10	0.5	1	22
converters (C)	C[e]	NA[g]	NA[g]	120	240	22
Concentrate dryer (CD) followed	CD	5	10	0.5	1	21-22
by Noranda reactors (NR) and	NR	NA	NA	NA	NA	
converters (C)	C	NA	NA	NA	NA	

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[a] Expressed as units/unit weight of concentrated ore processed by the smelter. Approximately 4 unit weights of concentrate are required to produce 1 unit weight of blister copper. NA = not available.

[b] For particulate matter removal, gaseous effluents from roasters, smelting furnaces and converters usually are treated in hot ESPs at 200 to 340°C (400 to 650°F) or in cold ESPs with gases cooled to about 120°C (250°F) before ESP. Particulate emissions from copper smelters contain volatile metallic oxides which remain in vapor form at higher temperatures (120°C or 250°F). Therefore, overall particulate removal in hot ESPs may range 20 to 80% and in cold ESPs may be 99%. Converter gas effluents and, at some smelters, roaster gas effluents are treated in single contact acid plants (SCAP) or double contact acid plants (DCAP) for SO_2 removal. Typical SCAPs are about 96% efficient, and DCAPs are up to 99.8% efficient in SO_2 removal. They also remove over 99% of particulate matter. Noranda and flash furnace offgases are also processed through acid plants and are subject to the same collection efficiencies as cited for converters and some roasters.

[c] In addition to sources indicated, each smelter configuration contains fire refining anode furnaces after the converters. Anode furnaces emit negligible SO_2. No particulate emission data are available for anode furnaces.

[d] Factors for all configurations except reverberatory furnace followed by converters have been developed by normalizing test data for several smelters to represent 30% sulfur content in concentrated ore.

[e] Based on the test data for the configuration multiple hearth roaster followed by reverberatory furnace and converters.

[f] Used to recover copper from furnace slag and converter slag.

[g] Since converters at flash furnace and Noranda furnace smelters treat high copper content matte, converter particulate emissions from flash furnace smelters are expected to be lower than those from conventional smelters with multiple hearth roasters, reverberatory furnace and converters.

TABLE 7.3-3. PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR MULTIPLE HEARTH ROASTER AND REVERBERATORY SMELTER OPERATIONS[a]

EMISSION FACTOR RATING: D

	Cumulative mass % ≤ stated size		Cumulative emission factors			
Particle size[b] (um)	Uncontrolled	ESP controlled	Uncontrolled Kg/Mg	Uncontrolled lb/ton	ESP controlled[c] Kg/Mg	ESP controlled[c] lb/ton
15	100	100	47	95	0.47	0.95
10	100	99	47	94	0.47	0.94
5	100	98	47	93	0.46	0.93
2.5	97	84	46	80	0.40	0.80
1.25	66	76	31	72	0.36	0.72
0.625	25	62	12	59	0.29	0.59
Total	100	100	47	95	0.47	0.95

[a] Reference 25. Expressed as units/unit weight of concentrated ore processed by the smelter.

[b] Expressed as aerodynamic equivalent diameter.

[c] Nominal particulate removal efficiency is 99%.

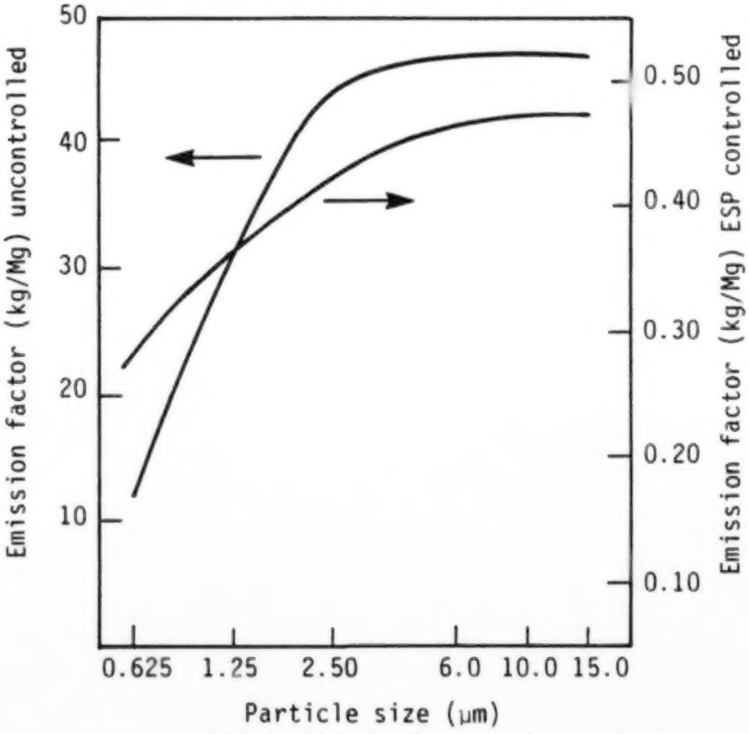

Figure 7.3-2. Size specific emission factors for multiple hearth roaster and reverberatory smelter.

TABLE 7.3-4. PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR REVERBERATORY SMELTER OPERATIONS[a]

EMISSION FACTOR RATING: E

	Cumulative mass % $\leq$ stated size		Cumulative emission factors			
Particle size[b] (um)	Uncontrolled	ESP controlled	Uncontrolled		ESP controlled[c]	
			Kg/Mg	lb/ton	Kg/Mg	lb/ton
15	NR	83	NR	NR	0.21	0.42
10	27	78	6.8	13.6	0.20	0.40
5	23	69	5.8	11.6	0.18	0.36
2.5	21	56	5.3	10.6	0.14	0.28
1.25	16	40	4.0	8.0	0.10	0.20
0.625	9	32	2.3	4.6	0.08	0.16
Total	100	100	25	50	0.25	0.50

[a] Reference 25. Expressed as units/unit weight of concentrated ore processed by the smelter. NR = not reported because of excessive extrapolation.

[b] Expressed as aerodynamic equivalent diameter.

[c] Nominal particulate removal efficiency is 99%.

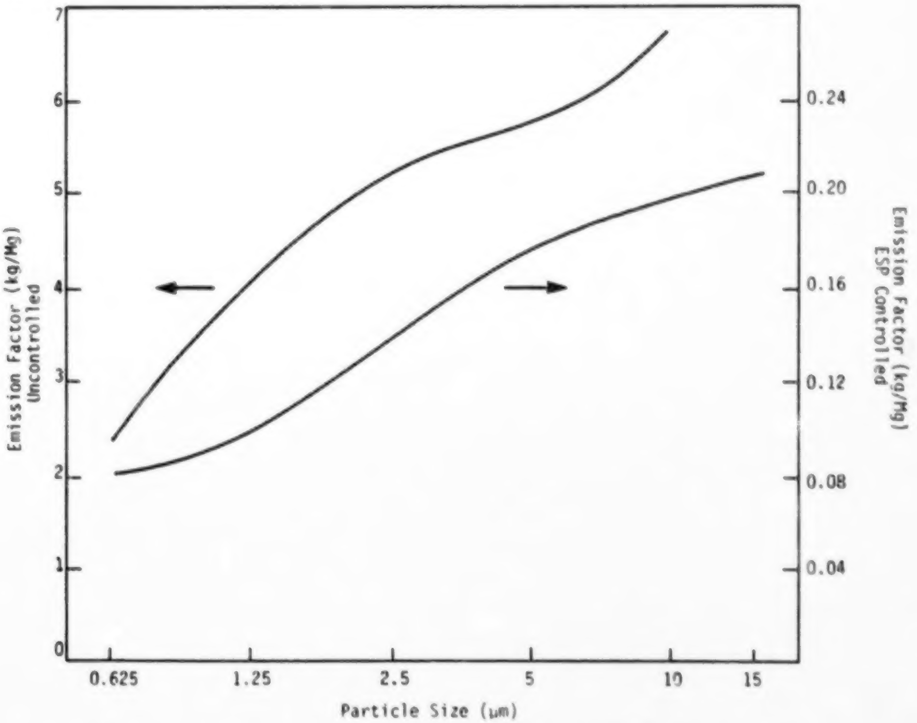

Figure 7.3-3. Size specific emission factors for reverberatory smelting.

TABLE 7.3-5. PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR COPPER CONVERTER OPERATIONS[a]

EMISSION FACTOR RATING: E

	Cumulative mass % ≤ stated size		Cumulative emission factors			
Particle size[b] (um)	Uncontrolled	ESP controlled	Uncontrolled		ESP controlled[c]	
			Kg/Mg	lb/ton	Kg/Mg	lb/ton
15	NR	100	NR	NR	0.18	0.36
10	59	99	10.6	21.2	0.17	0.36
5	32	72	5.8	11.5	0.13	0.26
2.5	12	56	2.2	4.3	0.10	0.20
1.25	3	42	0.5	1.1	0.08	0.15
0.625	1	30	0.2	0.4	0.05	0.11
Total	100	100	18	36	0.18	0.36

[a] Reference 25. Expressed as units/unit weight of concentrated ore processed by the smelter. NR = not reported because of excessive extrapolation.
[b] Expressed as aerodynamic equivalent diameter.
[c] Nominal particulate removal efficiency is 99 %.

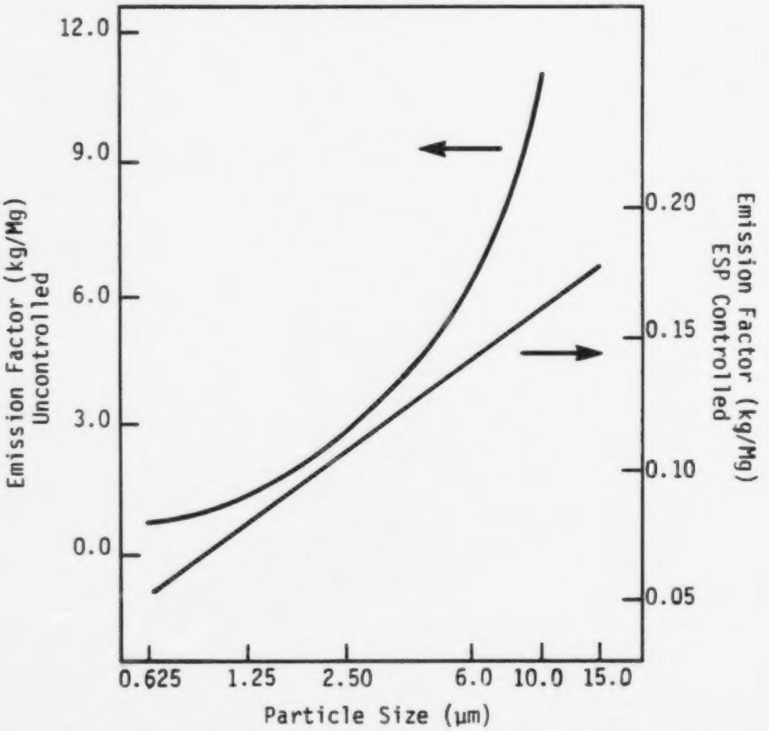

Figure 7.3-4. Size specific emission factors for copper converting.

Fugitive emissions are generated during the discharge and transfer of hot calcine from multiple hearth roasters, with negligible amounts possible from the charging of these roasters. Fluid bed roasting, a closed loop operation, has negligible fugitive emissions.

Matte tapping and slag skimming operations are sources of fugitive emissions from smelting furnaces. Fugitive emissions can also result from charging of a smelting furnace or from leaks, depending upon the furnace type and condition. A typical single matte tapping operation lasts from 5 to 10 minutes and a single slag skimming operation lasts from 10 to 20 minutes. Tapping frequencies vary with furnace capacity and type. In an 8 hour shift, matte is tapped 5 to 20 times, and slag is skimmed 10 to 25 times.

Each of the various stages of converter operation - the charging, blowing, slag skimming, blister pouring, and holding - is a potential source of fugitive emissions. During blowing, the converter mouth is in stack (i. e., a close fitting primary hood is over the mouth to capture offgases). Fugitive emissions escape from the hoods. During charging, skimming and pouring operations, the converter mouth is out of stack (i. e., the converter mouth is rolled out of its vertical position, and the primary hood is isolated). Fugitive emissions are discharged during rollout.

TABLE 7.3-6. FUGITIVE EMISSION FACTORS FOR PRIMARY COPPER SMELTERS[a]

EMISSION FACTOR RATING: B

Source of emission	Particulate		SO_2	
	kg/Mg	lb/ton	kg/Mg	lb/ton
Roaster calcine discharge	1.3	2.6	0.5	1
Smelting furnace[b]	0.2	0.4	2	4
Converter	2.2	4.4	65	130
Converter slag return	NA	NA	0.05	0.1
Anode furnace	0.25	0.5	0.05	0.1
Slag cleaning furnace[c]	4	8	3	6

[a] References 16,22,25-32. Expressed as mass units/unit weight of concentrated ore processed by the smelter. Approximately 4 unit weights of concentrate are required to produce 1 unit weight of copper metal. Factors for flash furnace smelters and Noranda furnace smelters may be lower than reported values. NA = not available.

[b] Includes fugitive emissions from matte tapping and slag skimming operations. About 50% of fugitive particulate emissions and about 90% of total SO_2 emissions are from matte tapping operations, with remainder from slag skimming.

[c] Used to treat slags from smelting furnaces and converters at the flash furnace smelter.

TABLE 7.3-7. UNCONTROLLED PARTICLE SIZE AND SIZE SPECIFIC EMISSION FACTORS FOR FUGITIVE EMISSIONS FROM REVERBERATORY FURNACE MATTE TAPPING OPERATIONS[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	76	0.076	0.152
10	74	0.074	0.148
5	72	0.072	0.144
2.5	69	0.069	0.138
1.25	67	0.067	0.134
0.625	65	0.065	0.130
Total	100	0.100	0.200

[a] Reference 25. Expressed as units/unit weight of concentrated ore processed by the smelter.

[b] Expressed as aerodynamic equivalent diameter.

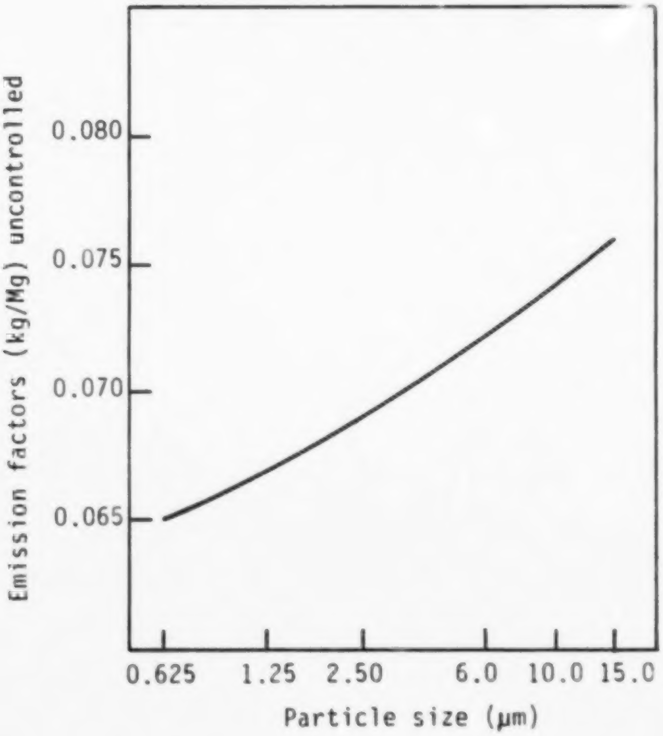

Figure 7.3-5. Size specific fugitive emission factors for reverberatory furnace matte tapping operations.

TABLE 7.3-8. PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR FUGITIVE EMISSIONS FROM REVERBERATORY FURNACE SLAG TAPPING OPERATIONS[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	33	0.033	0.066
10	28	0.028	0.056
5	25	0.025	0.050
2.5	22	0.022	0.044
1.25	20	0.020	0.040
0.625	17	0.017	0.034
Total	100	0.100	0.200

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[a] Reference 25. Expressed as units/unit weight of concentrated ore processed by the smelter.

[b] Expressed as aerodynamic equivalent diameter.

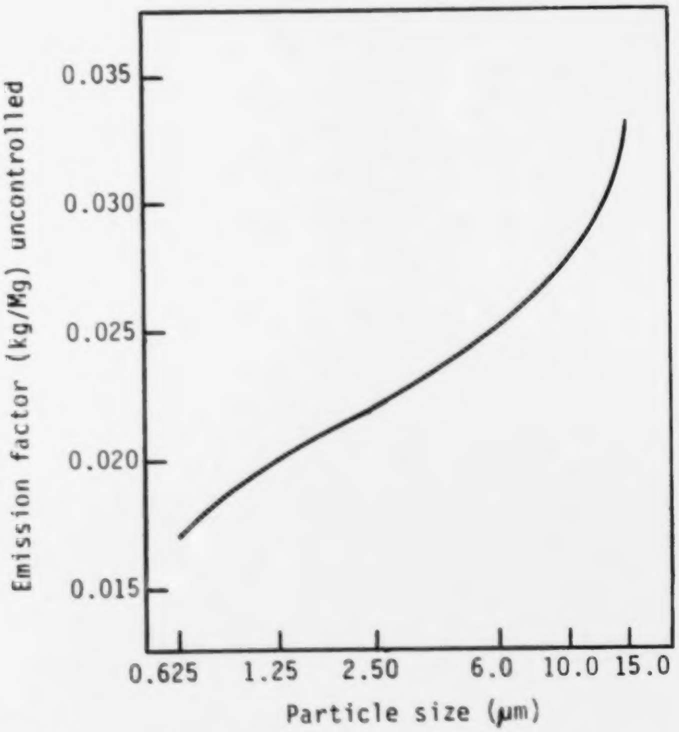

Figure 7.3-6. Size specific fugitive emission factors for reverberatory furnace slag tapping operations.

TABLE 7.3-9. PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR FUGITIVE EMISSIONS FROM CONVERTER SLAG AND COPPER BLOW OPERATIONS[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	98	2.2	4.3
10	96	2.1	4.2
5	87	1.9	3.8
2.5	60	1.3	2.6
1.25	47	1.0	2.1
0.625	38	0.8	1.7
Total	100	2.2	4.4

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[a] Reference 25. Expressed as units/unit weight of concentrated ore processed by the smelter.

[b] Expressed as aerodynamic equivalent diameter.

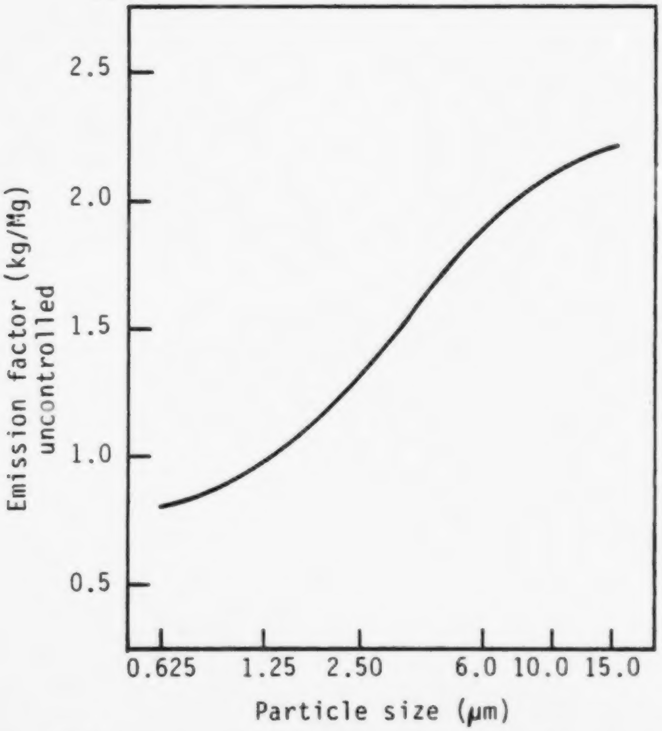

Figure 7.3-7. Size specific fugitive emission factors for converter slag and copper blow operations.

At times during normal smelting operations, slag or blister copper can not be transferred immediately from or to the converters. This condition, holding stage, may occur for several reasons, including insufficient matte in the smelting furnace, the unavailability of a crane, and others. Under these conditions, the converter is rolled out of its vertical position and remains in a holding position and fugitive emissions may result.

7.3.4 Lead Emissions

At primary copper smelters, both process emissions and fugitive particulate from various pieces of equipment contain oxides of many inorganic elements, including lead. The lead content of particulate emissions depends upon both the lead content of the smelter feed and the process offgas temperature. Lead emissions are effectively removed in particulate control systems operating at low temperatures, about 120°C (250°F).

Table 7.3-10 presents process and fugitive lead emission factors for various operations of primary copper smelters.

TABLE 7.3-10. LEAD EMISSION FACTORS FOR PRIMARY COPPER SMELTERS[a]

EMISSION FACTOR RATING: C

Operation	Emission factor[b]	
	kg/Mg	lb/ton
Roasting	0.075	0.15
Smelting	0.036	0.072
Converting	0.13	0.27
Refining	NA	NA

[a] Reference 33. Expressed as units/unit weight of concentrated ore processed by smelter. Approximately four unit weights of concentrate are required to produce one unit weight of copper metal. Based on test data for several smelters with 0.1 to 0.4 % lead in feed throughput. NA = not available.

[b] For process and fugitive emissions totals.

[c] Based on test data on multihearth roasters. Includes total of process emissions and calcine transfer fugutive emissions. The latter are about 10% of total process and fugitive emissions.

[d] Based on test data on reverberatory furnaces. Includes total process emissions and fugitive emissions from matte tapping and slag skimming operations. Fugitive emissions from matte tapping and slag skimming operations amount to about 35% and 2%, respectively.

[e] Includes total of process and fugitive emissions. Fugitives constitute about 50% of total.

Fugitive emissions from primary copper smelters are captured by applying either local ventilation or general ventilation techniques. Once captured, emissions may be vented directly to a collection device or be combined with process offgases before collection. Close fitting exhaust hood capture systems are used for multiple hearth roasters and hood ventilation systems for smelt matte tapping and slag skimming operations. For converters, secondary hood systems or building evacuation systems are used.

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AP-42 Section 7.6

Primary Lead Smelting

7.6 PRIMARY LEAD SMELTING

7.6.1 Process Description

Lead is usually found naturally as a sulfide ore containing small amounts of copper, iron, zinc and other trace elements. It is usually concentrated at the mine from an ore of 3 to 8 percent lead to a concentrate of 55 to 70 percent lead, containing from 13 to 19 weight percent free and uncombined sulfur. Processing involves three major steps, sintering, reduction and refining.

A typical diagram of the production of lead metal from ore concentrate, with particle and gaseous emission sources indicated, is shown in Figure 7.6-1.

Sintering - Sinter is produced by a sinter machine, a continuous steel pallet conveyor belt moved by gears and sprockets. Each pallet consists of perforated or slotted grates, beneath which are wind boxes connected to fans to provide a draft, either up or down, through the moving sinter charge. Except for draft direction, all machines are similar in design, construction and operation.

The primary reactions occurring during the sintering process are autogenous, occurring at approximately 1000°C (1800°F):

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2 \qquad (1)$$

$$PbS + 2O_2 \longrightarrow PbSO_4 \qquad (2)$$

Operating experience has shown that system operation and product quality are optimum when the sulfur content of the sinter charge is from 5 to 7 weight percent. To maintain this desired sulfur content, sulfide free fluxes such as silica and limestone, plus large amounts of recycled sinter and smelter residues, are added to the mix. The quality of the product sinter is usually determined by its Ritter Index hardness, which is inversely proportional to the sulfur content. Hard quality sinter (low sulfur content) is preferred, because it resists crushing during discharge from the sinter machine. Undersize sinter, usually from insufficient desulfurization, is recycled for further processing.

Of the two kinds of sintering machines, the updraft design is superior for many reasons. First, the sinter bed is more permeable (and hence can be larger), thereby permitting a higher production rate than with a downdraft machine of similar dimensions. Secondly, the small amounts of elemental lead that form during sintering will solidify at their point of formation in updraft machines, but, in downdraft operation, the metal flows down and collects on the grates or at the bottom of the sinter charge, thus causing increased pressure drop and attendant reduced blower capacity. The updraft system also can produce sinter

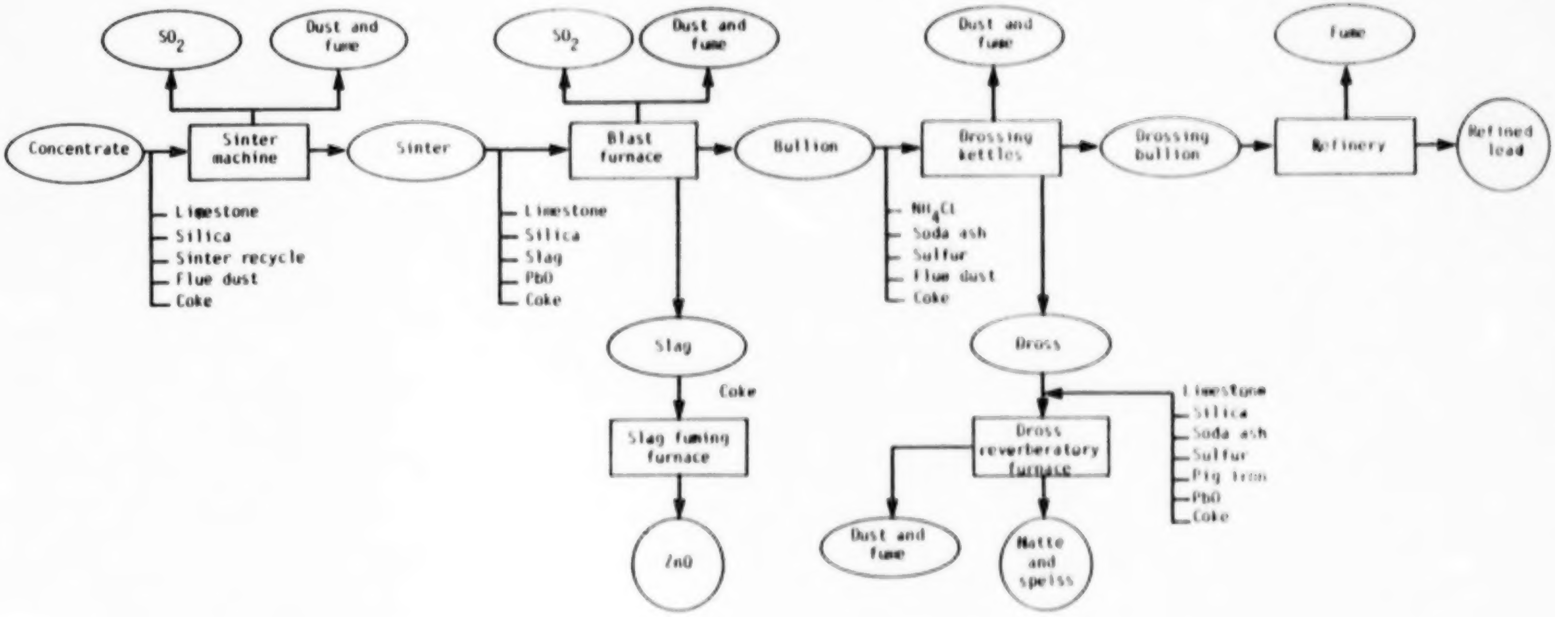
SO$_2$
Dust and fume
SO$_2$
Dust and fume
Dust and fume
Fume
Concentrate
Sinter machine
Sinter
Blast furnace
Bullion
Drossing kettles
Drossing bullion
Refinery
Refined lead
Limestone
Silica
Sinter recycle
Flue dust
Coke
Limestone
Silica
Slag
PbO
Coke
NH$_4$Cl
Soda ash
Sulfur
Flue dust
Coke
Slag
Dross
Coke
Slag fuming furnace
Dross reverberatory furnace
Limestone
Silica
Soda ash
Sulfur
Pig iron
PbO
Coke
ZnO
Dust and fume
Matte and speiss

Figure 7.6-1. Typical primary lead processing scheme.

of higher lead content, and it requires less maintenance than the downdraft machine. Finally, and most important from an air pollution control standpoint, updraft sintering can produce a single strong sulfur dioxide (SO_2) effluent stream from the operation, by the use of weak gas recirculation. This permits more efficient and economical use of control methods such as sulfuric acid recovery devices.

Reduction - Lead reduction is carried out in a blast furnace, which basically is a water jacketed shaft furnace supported by a refractory base. Tuyeres, through which combustion air is admitted under pressure, are located near the bottom and are evenly spaced on either side of the furnace.

The furnace is charged with a mixture of sinter (80 to 90 percent of charge), metallurgical coke (8 to 14 percent of charge), and other materials such as limestone, silica, litharge, slag forming constituents, and various recycled and cleanup materials. In the furnace, the sinter is reduced to lead bullion by Reactions 3 through 7.

$$C + O_2 \rightarrow CO_2 \tag{3}$$

$$C + CO_2 \rightarrow 2CO \tag{4}$$

$$PbO + CO \rightarrow Pb + CO_2 \tag{5}$$

$$2PbO + PbS \rightarrow 3Pb + SO_2 \tag{6}$$

$$PbSO_4 + PbS \rightarrow 2Pb + 2SO_2 \tag{7}$$

Carbon monoxide and heat required for reduction are supplied by the combustion of coke. Most of the impurities are eliminated in the slag. Solid products from the blast furnace generally separate into four layers, speiss (the lightest material, basically arsenic and antimony), matte (copper sulfide and other metal sulfides), slag (primarily silicates), and lead bullion. The first three layers are called slag, which is continually collected from the furnace and is either processed at the smelter for its metal content or shipped to treatment facilities.

Sulfur oxides are also generated in blast furnaces from small quantities of residual lead sulfide and lead sulfates in the sinter feed. The quantity of these emissions is a function not only of the sinter's residual sulfur content, but also of the sulfur captured by copper and other impurities in the slag.

Rough lead bullion from the blast furnace usually requires preliminary treatment (drossing) in kettles before undergoing refining operations. First, the bullion is cooled to 370° to 430°C (700 to 800°F). Copper and small amounts of sulfur, arsenic, antimony and nickel collect on the surface as a dross and are removed from the solution. This dross, in turn, is treated in a reverberatory furnace to concentrate the copper and other metal impurities before being routed to copper smelters for their eventual recovery. To enhance copper removal, drossed lead bullion is treated by adding sulfur bearing material, zinc, and/or aluminum, lowering the copper content to approximately 0.01 percent.

Refining - The third and final phase in smelting, the refining of the bullion in cast iron kettles, occurs in five steps:

- Removal of antimony, tin and arsenic
- Removal of precious metals by Parke's Process, in which zinc combines with gold and silver to form an insoluble intermetallic at operating temperatures
- Vacuum removal of zinc
- Removal of bismuth by the Betterson Process, which is the addition of calcium and magnesium to form an insoluble compound with the bismuth that is skimmed from the kettle
- Removal of remaining traces of metal impurities by addition of NaOH and $NaNO_3$

The final refined lead, commonly from 99.990 to 99.999 percent pure, is then cast into 45 kilogram (100 pound) pigs for shipment.

7.6.2 Emissions And Controls[1-2]

Each of the three major lead smelting process steps generates substantial quantities of SO_2 and/or particulate.

Nearly 85 percent of the sulfur present in the lead ore concentrate is eliminated in the sintering operation. In handling process offgases, either a single weak stream is taken from the machine hood at less than 2 percent SO_2, or two streams are taken, a strong stream (5 to 7 percent SO_2) from the feed end of the machine and a weak stream (less than 0.5 percent SO_2) from the discharge end. Single stream operation has been used if there is little or no market for recovered sulfur, so that the uncontrolled, weak SO_2 stream is emitted to the atmosphere. When sulfur removal is required, however, dual stream operation is preferred. The strong stream is sent to a sulfuric acid plant, and the weak stream is vented to the atmosphere after removal of particulate.

When dual gas stream operation is used with updraft sinter machines, the weak gas stream can be recirculated through the bed to mix with the strong gas stream, resulting in a single stream with an SO_2 concentration of about 6 percent. This technique decreases machine production capacity, but it does permit a more convenient and economical recovery of the SO_2 by sulfuric acid plants and other control methods.

Without weak gas recirculation, the end portion of the sinter machine acts as a cooling zone for the sinter and, consequently, assists in the reduction of dust formation during product discharge and screening. However, when recirculation is used, sinter is usually discharged at 400° to 500°C (745° to 950°F), with an attendant increase in particulate. Methods to reduce these dust quantities include recirculatng offgases through the sinter bed (to use the bed as a filter) or ducting gases from the sinter machine discharge through a particulate collection device and then to the atmosphere. Because reaction activity has ceased in the discharge area, these gases contain little SO_2.

Particulate emissions from sinter machines range from 5 to 20 percent of the concentrated ore feed. In terms of product weight, a typical emission is estimated to be 106.5 kilograms per megagram (213 pounds per ton) of lead produced. This value, and other particulate and SO_2 factors, appears in Table 7.6-1.

Typical material balances from domestic lead smelters indicate that about 15 percent of the sulfur in the ore concentrate fed to the sinter machine is eliminated in the blast furnace. However, only half of this amount, about 7 percent of the total sulfur in the ore, is emitted as SO_2.

The remainder is captured by the slag. The concentration of this SO_2 stream can vary from 1.4 to 7.2 grams per cubic meter (500 to 2500 parts per million) by volume , depending on the amount of dilution air injected to oxidize the carbon monoxide and to cool the stream before baghouse particulate removal.

Particulate emissions from blast furnaces contain many different kinds of material, including a range of lead oxides, quartz, limestone, iron pyrites, iron-lime-silicate slag, arsenic, and other metallic compounds associated with lead ores. These particles readily agglomerate and are primarily submicron in size, difficult to wet, and cohesive. They will bridge and arch in hoppers. On average, this dust loading is quite substantial, as is shown in Table 7.6-1.

Minor quantities of particulates are generated by ore crushing and materials handling operations, and these emission factors are also presented in Table 7.6-1.

TABLE 7.6-1. UNCONTROLLED EMISSION FACTORS FOR PRIMARY LEAD SMELTING[a]

EMISSION FACTOR RATING: B

Process	Particulate		Sulfur dioxide	
	kg/Mg	lb/ton	kg/Mg	lb/ton
Ore crushing[b]	1.0	2.0	-	-
Sintering (updraft)[c]	106.5	213.0	275.0	550.0
Blast furnace[d]	180.5	361.0	22.5	45.0
Dross reverberatory furnace[e]	10.0	20.0	Neg	Neg
Materials handling[f]	2.5	5.0	-	-

[a] Based on quantity of lead produced. Dash = no data. Neg = negligible.
[b] Reference 2. Based on quantity of ore crushed. Estimated from similar nonferrous metals processing.
[c] References 1, 5-7.
[d] References 1-2, 8.
[e] Reference 2.
[f] Reference 2. Based on quantity of materials handled.

Table 7.6-2 and Figure 7.6-2 present size specific emission factors for the controlled emissions from a primary lead blast furnace. No other size distribution data can be located for point sources within a primary lead processing plant. Lacking definitive data, size distributions for uncontrolled assuming that the uncontrolled size distributions for the sinter machine and blast furnace are the same as for fugitive emissions from these sources.

Tables 7.6-3 through 7.6-7 and Figures 7.6-3 through 7.6-7 present size specific emission factors for the fugitive emissions generated at a primary lead processing plant. The size distribution of fugitive emissions at a primary lead processing plant is fairly uniform, with approximately 79 percent of these emissions at less than 2.5 micrometers. Fugitive emissions less than 0.625 micrometers in size make up approximately half of all fugitive emissions, except from the sinter machine, where they constitute about 73 percent.

Emission factors for total fugitive particulate from primary lead smelting processes are presented in Table 7.6-8. The factors are based on a combination of engineering estimates, test data from plants currently operating, and test data from plants no longer operating. The values should be used with caution, because of the reported difficulty in accurately measuring the source emission rates.

Emission controls on lead smelter operations are for particulate and sulfur dioxide. The most commonly employed high efficiency particulate control devices are fabric filters and electrostatic precipitators (ESP), which often follow centrifugal collectors and tubular coolers (pseudogravity collectors).

Three of the six lead smelters presently operating in the United States use single absorption sulfuric acid plants to control SO_2 emissions from sinter machines and, occasionally, from blast furnaces. Single stage plants can attain sulfur oxide levels of 5.7 grams per cubic meter (2000 parts per million), and dual stage plants can attain levels of 1.6 grams per cubic meter (550 parts per million). Typical efficiencies of dual stage sulfuric acid plants in removing sulfur oxides can exceed 99 percent. Other technically feasible SO_2 control methods are elemental sulfur recovery plants and dimethylaniline (DMA) and ammonia absorption processes. These methods and their representative control efficiencies are given in Table 7.6-9.

TABLE 7.6-2. LEAD EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR BAGHOUSE CONTROLLED BLAST FURNACE FLUE GASES[a]

EMISSION FACTOR RATING: C

Particle size[b] (um)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	98	1.17	2.34
10	86.3	1.03	2.06
6	71.8	0.86	1.72
2.5	56.7	0.68	1.36
1.25	54.1	0.65	1.29
1.00	53.6	0.64	1.28
0.625	52.9	0.63	1.27
Total	100.0	1.20	2.39

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[a] Reference 9.

[b] Expressed as aerodynamic equivalent diameter.

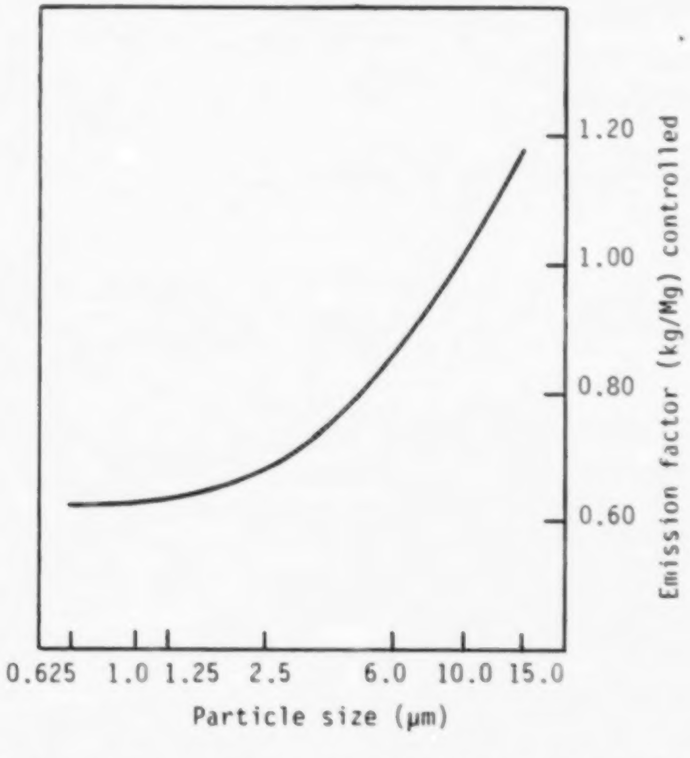

Figure 7.6-2. Size specific emission factors for baghouse controlled blast furnace.

TABLE 7.6-3 UNCONTROLLED FUGITIVE EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR LEAD ORE STORAGE[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	91	0.011	0.023
10	86	0.010	0.021
6	80.5	0.010	0.020
2.5	69.0	0.009	0.017
1.25	61.0	0.008	0.015
1.00	59.0	0.007	0.015
0.625	54.5	0.007	0.013
Total	100.0	0.012	0.025

[a] Reference 10.

[b] Expressed as aerodynamic equivalent diameter.

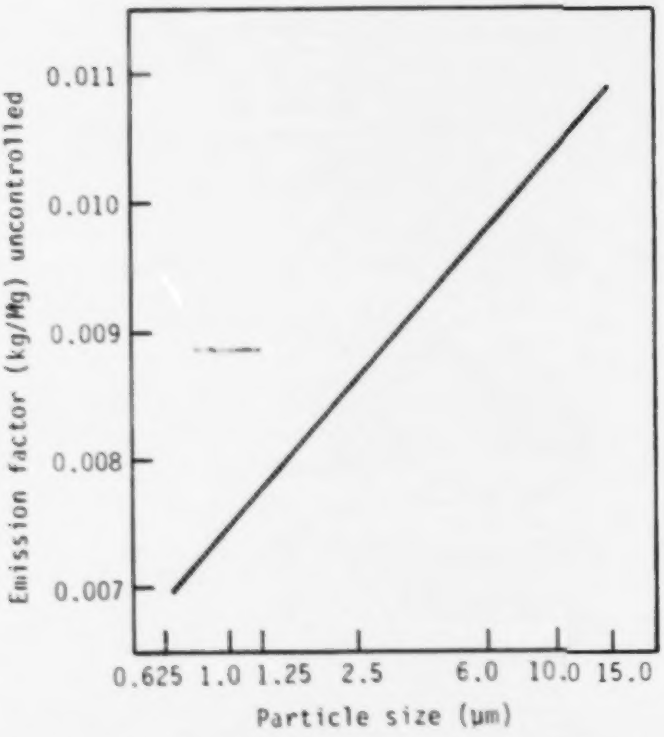

Figure 7.6-3. Size specific uncontrolled fugitive emission factors for lead ore storage.

TABLE 7.6-4. UNCONTROLLED LEAD FUGITIVE EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR SINTER MACHINE[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	99	0.10	0.19
10	98	0.10	0.19
6	94.1	0.09	0.17
2.5	87.3	0.08	0.16
1.25	81.1	0.07	0.15
1.00	78.4	0.07	0.15
0.625	73.2	0.07	0.14
Total	100.0	0.10	0.19

---

[a] Reference 10.

[b] Expressed as aerodynamic equivalent diameter.

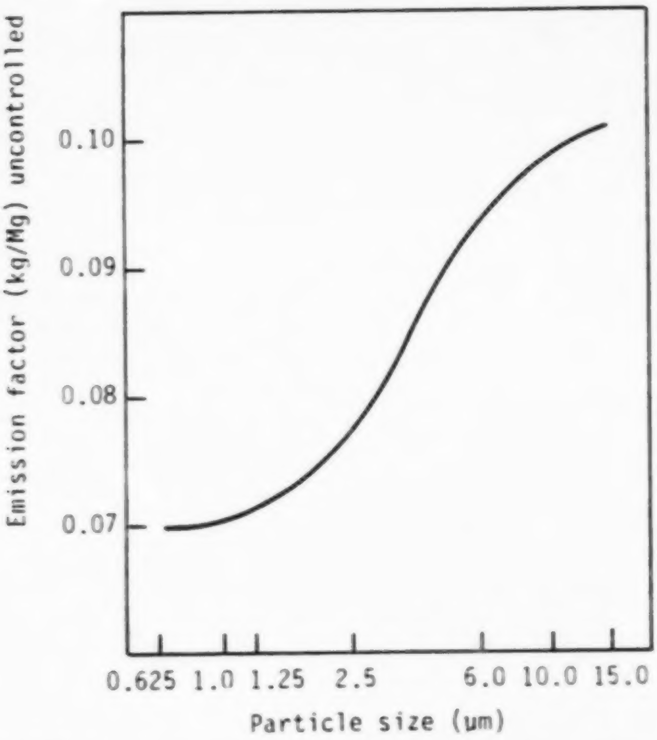

Figure 7.6-4. Size specific fugitive emission factors for uncontrolled sinter machine.

TABLE 7.6-5. UNCONTROLLED LEAD FUGITIVE EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR BLAST FURNACE[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤ stated size	Cumulative emission factors kg/Mg	Cumulative emission factors lb/ton
15	94	0.11	0.23
10	89	0.11	0.21
6	83.5	0.10	0.20
2.5	73.8	0.09	0.17
1.25	65.0	0.08	0.15
1.00	61.8	0.07	0.15
0.625	54.4	0.06	0.13
Total	100.0	0.12	0.24

[a] Reference 10.

[b] Expressed as aerodynamic equivalent diameter.

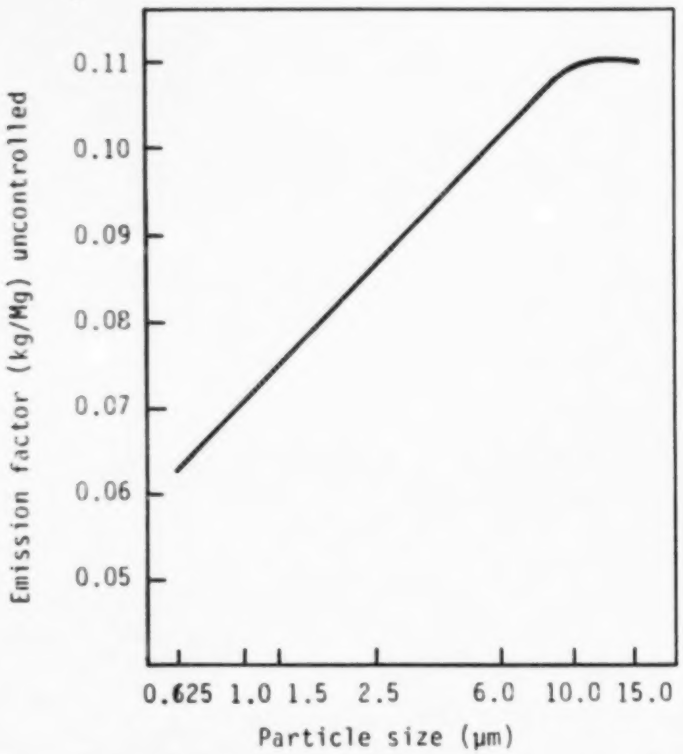

Figure 7.6-5. Size specific lead fugitive emission factors for uncontrolled blast furnace.

TABLE 7.6-6. UNCONTROLLED LEAD FUGITIVE EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR DROSS KETTLE[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤ stated size	Cumulative emission factors kg/Mg	Cumulative emission factors lb/ton
15	99	0.18	0.36
10	98	0.18	0.35
6	92.5	0.17	0.33
2.5	83.3	0.15	0.30
1.25	71.3	0.13	0.26
1.00	66.0	0.12	0.24
0.625	51.0	0.09	0.18
Total	100.0	0.18	0.36

[a] Reference 10.

[b] Expressed as aerodynamic equivalent diameter.

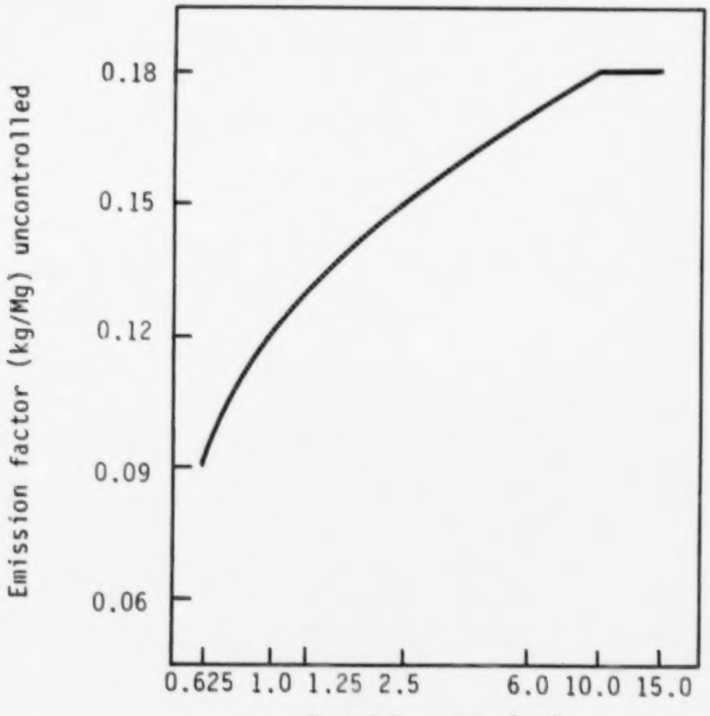

Figure 7.6-6. Size specific lead fugitive emission factors for uncontrolled dross kettle.

TABLE 7.6-7. UNCONTROLLED LEAD FUGITIVE EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR REVERBERATING FURNACE[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤ stated size	Cumulative emission factors kg/Mg	Cumulative emission factors lb/ton
15	99	0.24	0.49
10	98	0.24	0.48
6	92.3	0.22	0.45
2.5	80.8	0.20	0.39
1.25	67.5	0.16	0.33
1.00	61.8	0.15	0.30
0.625	49.3	0.12	0.24
Total	100.0	0.24	0.49

[a] Reference 10.

[b] Expressed as aerodynamic equivalent diameter.

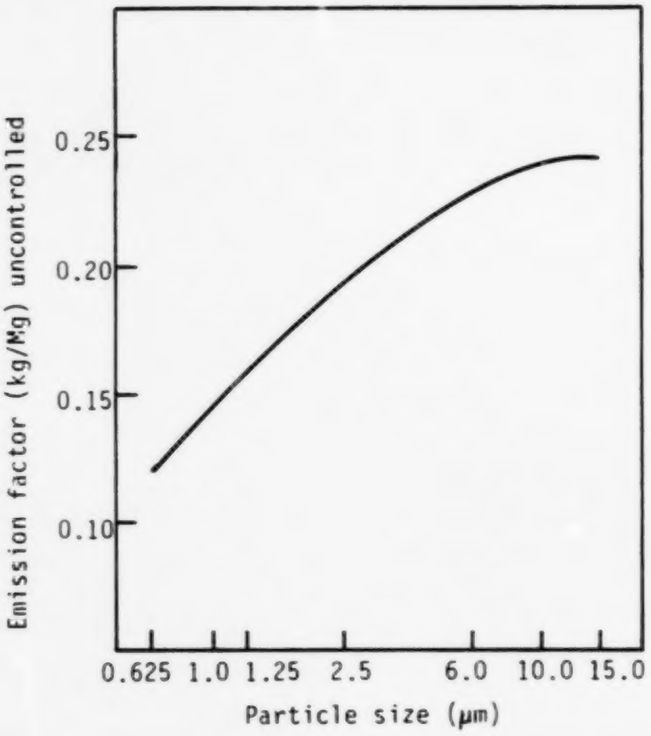

Figure 7.6-7. Size specific lead fugitive emission factors for uncontrolled reverberating furnace.

TABLE 7.6-8. UNCONTROLLED FUGITIVE EMISSION FACTORS FOR PRIMARY LEAD SMELTING PROCESSESS[a,b]

Emission points	Particulate		Emission Factor Rating
	kg/Mg	lb/ton	
Ore storage[b]	0.012	0.025	D
Ore mixing and pelletizing (crushing)	1.13	2.26	E
Car charging (conveyor loading, transfer) of sinter	0.25	0.50	E
Sinter machine			
Machine leakage[c]	0.34	0.68	E
Sinter return handling	4.50	9.00	E
Machine discharge, sinter crushing, screening[c]	0.75	1.50	E
Sinter transfer to dump area	0.10	0.20	E
Sinter product dump area	0.005	0.01	E
Total building[b]	0.10	0.19	D
Blast furnace			
Lead pouring to ladle, transferring, slag pouring[c]	0.47	0.93	D
Slag cooling[d]	0.24	0.47	E
Zinc fuming furnace vents	2.30	4.60	E
Dross kettle[b]	0.24	0.48	D
Reverberatory furnace leakage[b]	1.50	3.00	D
Silver retort building	0.90	1.80	E
Lead casting	0.44	0.87	E

[a] Expressed in units/end product lead produced, except sinter operations, which are units/sinter handled, transferred, charged.

[b] Reference 10.

[c] References 12-13. Engineering judgment, using steel sinter machine leakage emission factor.

[d] Reference 2. Engineering judgment, estimated to be half the magnitude of lead pouring and ladling operations.

TABLE 7.6-9. TYPICAL CONTROL DEVICE EFFICIENCIES IN PRIMARY LEAD SMELTING OPERATIONS

Control method	Efficiency range (%)	
	Particulate	Sulfur dioxide
Centrifugal collector[a]	80 - 90	NA
Electrostatic precipitator[a]	95 - 99	NA
Fabric filter[a]	95 - 99	NA
Tubular cooler (associated with waste heat boiler)[a]	70 - 80	NA
Sulfuric acid plant (single contact)[b,c]	99.5 - 99.9	96 - 97
Sulfuric acid plant (dual contact)[b,d]	99.5 - 99.9	96 - 99.9
Elemental sulfur recovery plant[b,e]	NA	90
Dimethylaniline (DMA) absorption process[b,c]	NA	95 - 99
Ammonia absorption process[b,f]	NA	92 - 95

[a] Reference 2. NA = not available.

[b] Reference 1.

[c] High particulate control efficiency from action of acid plant gas cleaning systems. With SO_2 inlet concentrations 5-7%, typical outlet emission levels are 5.7 g/m^3 (2000 ppm) for single contact, 1.4 g/m^3 (500 ppm) for dual contact.

[d] Collection efficiency for a two stage uncontrolled Claus type plant. See Section 5.18, Sulfur Recovery.

[e] With SO_2 inlet concentrations 4-6 %, typical outlet emission levels are from 1.4-8.6 g/m^3 (500-3000 ppm).

[f] With SO_2 inlet concentrations of 1.5-2.5 %, typical outlet emission level is 3.4 g/m^3 (1200 ppm).

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AP-42 Section 7.11

Secondary Lead Processing

7.11 SECONDARY LEAD PROCESSING

7.11.1 Process Description[1-7]

The secondary lead industry processes a variety of lead bearing scrap and residue to produce lead and lead alloy ingots, battery lead oxide, and lead pigments (Pb_3O_4 and PbO). Processing may involve scrap pretreatment, smelting, and refining/casting. Processes typically used in each operation are shown in Figure 7.11-1.

Scrap pretreatment is the partial removal of metal and nonmetal contaminants from leadbearing scrap and residue. Processes used for scrap pretreatment include battery breaking, crushing and sweating. Battery breaking is the draining and crushing of batteries, followed by manual separation of the lead from nonmetallic materials. Oversize pieces of scrap and residues are usually put through jaw crushers. This separated lead scrap is then mixed with other scraps and is smelted in reverberatory or blast furnaces to separate lead from metals with higher melting points. Rotary gas or oil furnaces usually are used to process low lead content scrap and residue, while reverberatory furnaces are used to process high lead content scrap. The partially purified lead is periodically tapped from these furnaces for further processing in smelting furnaces or pot furnaces.

Smelting is the production of purified lead by melting and separating lead from metal and nonmetallic contaminants and by reducing oxides to elemental lead. Reverberatory smelting furnaces are used to produce a semisoft lead product that contains typically 3 to 4 percent antimony. Blast furnaces produce hard or antimonial lead containing about 10 percent antimony.

A reverberatory furnace,to produce semisoft lead, is charged with lead scrap, metallic battery parts, oxides, drosses, and other residues. The reverberatory furnace is a rectangular shell lined with refractory brick, and it is fired directly with oil or gas to a temperature of 1260°C (2300°F). The material to be melted is heated by direct contact with combustion gases. The average furnace can process about 45 megagrams per day (50 tons per day). About 47 percent of the charge is recovered as lead product and is periodically tapped into molds or holding pots. Forty-six percent of the charge is removed as slag and later processed in blast furnaces. The remaining 7 percent of the furnace charge escapes as dust or fume.

Blast furnaces produce hard lead from charges containing siliceous slag from previous runs (about 4.5 percent of the charge), scrap iron (about 4.5 percent), limestone (about 3 percent), and coke (about 5.5 percent). The reqaining 82.5 percent of the charge is comprised of oxides, pot furnace refining drosses, and reverberatory slag. The proportions of rerun slags, limestone, and coke, respectively vary to as high as 8 percent, 10 percent, and 8 percent of the charge. Processing capacity of the blast furnace ranges from 18 to 73 megagrams per day (20 to 80 tons per day). Similar to iron cupolas, the blast furnace is a vertical steel cylinder lined with refractory brick. Combustion

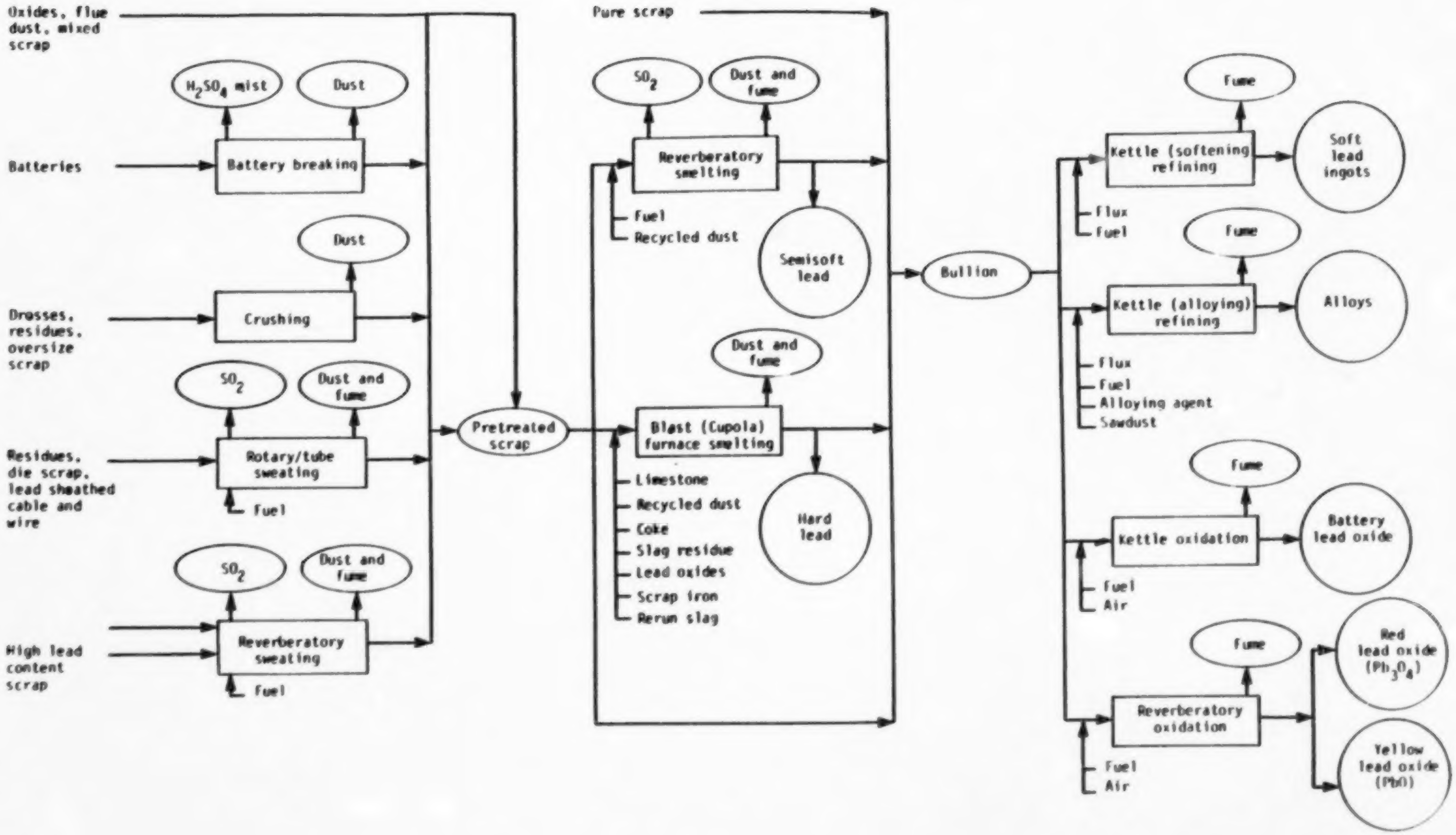
Oxides, flue dust, mixed scrap
Batteries
Drosses, residues, oversize scrap
Residues, die scrap, lead sheathed cable and wire
High lead content scrap
H_2SO_4 mist
Dust
Battery breaking
Dust
Crushing
SO_2
Dust and fume
Rotary/tube sweating
Fuel
SO_2
Dust and fume
Reverberatory sweating
Fuel
Pretreated scrap
Pure scrap
SO_2
Dust and fume
Reverberatory smelting
Fuel
Recycled dust
Semisoft lead
Dust and fume
Blast (Cupola) furnace smelting
Limestone
Recycled dust
Coke
Slag residue
Lead oxides
Scrap iron
Rerun slag
Hard lead
Bullion
Fume
Kettle (softening refining
Flux
Fuel
Soft lead ingots
Fume
Kettle (alloying) refining
Flux
Fuel
Alloying agent
Sawdust
Alloys
Fume
Kettle oxidation
Fuel
Air
Battery lead oxide
Fume
Reverberatory oxidation
Fuel
Air
Red lead oxide (Pb_3O_4)
Yellow lead oxide (PbO)

Figure 7.11-1. Typical secondary lead smelting and refining scheme.

air at 3.4 to 5.2 kilopascals (0.5 to 0.75 pounds per square inch) is introduced through tuyeres at the bottom of the furnace. Some of the coke combusts to melt the charge, while the remainder reduces lead oxides to elemental lead. The furnace exhaust is from 650° to 730°C (1200° to 1350°F).

As the lead charge melts, limestone and iron float to the top of the molte molten bath and form a flux that retards oxidation of the product lead. The molten lead flows from the furnace into a holding pot at a nearly continuous rate. The product lead constitutes roughly 70 percent of the charge. From the holding pot, the lead is usually cast into large ingots, called pigs, or sows.

About 18 percent of the charge is recovered as slag, with about 60 percent of this being a sulfurous slag called matte. Roughly 5 percent of the charge is retained for reuse, and the remaining 7 percent of the charge escapes as dust or fume.

Refining/casting is the use of kettle type furnaces for remelting, alloying, refining, and oxidizing processes. Materials charged for remelting are usually lead alloy ingots that require no further processing before casting. The furnaces used for alloying, refining and oxidizing are usually gas fired, and operating temperatures range from 370° to 480°C (700° to 900°F). Alloying furnaces simply melt and mix ingots of lead and alloy materials. Antimony, tin, arsenic, copper, and nickel are the most common alloying materials.

Refining furnaces are used either to remove copper and antimony for soft lead production, or to remove arsenic, copper and nickel for hard lead production. Sulfur may be added to the molten lead bath to remove copper. Copper sulfide skimmed off as dross may subsequently be processed in a blast furnace to recover residual lead. Aluminum chloride flux may be used to remove copper, antimony and nickel. The antimony content can be reduced to about 0.02 percent by bubbling air through the molten lead. Residual antimony can be removed by adding sodium nitrate and sodium hydroxide to the bath and skimming off the resulting dross. Dry drossing consists of adding sawdust to the agitated mass of molten metal. The sawdust supplies carbon to help separate globules of lead suspended in the dross and to reduce some of the lead oxide to elemental lead.

Oxidizing furnaces, either kettle or reverberatory units, are used to oxidize lead and to entrain the product lead oxides in the combustion air stream, with subsequent recovery in high efficiency baghouses.

7.11.2 Emissions And Controls[1,4-5]

Emission factors for controlled and uncontrolled processes and fugitive particulate are given in Tables 7.11-1 and 7.11-2. Particulate emissions from most processes are based on accumulated test data, whereas fugitive particulate emission factors are based on the assumption that 5 percent of uncontrolled stack emissions is released as fugitive emissions.

Reverberatory and blast furnaces account for the vast majority of the total lead emissions from the secondary lead industry. The relative quantities emitted from these two smelting processes can not be specified, because of a lack of complete information. Most of the remaining processes are small emission sources with undefined emission characteristics.

TABLE 7.11-1. EMISSION FACTORS FOR SECONDARY LEAD PROCESSING[a]

Pollutant		Sweating[b]	Leaching[c]	Smelting		Kettle refining	Kettle oxidation	Casting
				Reverberatory	Blast (cupola)[d]			
Particulate[e]								
Uncontrolled	(kg/Mg)	16-35	Neg[f]	162 (87-242)[g]	153 (92-207)[h]	0.02[j]	$\leq$20[k]	0.02[j]
	(lb/ton)	32-70	Neg[f]	323 (173-483)[m,g]	307 (184-413)[h]	0.03[j]	$\leq$40[k]	0.04[j]
Controlled	(kg/Mg)	-	Neg	0.50 (0.26-0.77)[m]	1.12 (0.11-2.44)[n]	Neg	-	Neg
	(lb/ton)	-	Neg	1.01 (0.53-1.55)[m]	2.24 (0.22-4.88)[n]	Neg	-	Neg
Lead[e]								
Uncontrolled	(kg/Mg)	4-8[p]	Neg	32 (17-48)[q]	52 (31-70)[r]	0.006[j]	-	0.007[j]
	(lb/ton)	7-16[p]	Neg	65 (35-97)[q]	104 (64-140)[r]	0.01[j]	-	0.01[j]
Controlled	(kg/Mg)	-	Neg	-	0.15 (0.02-0.32)[s]	Neg	-	Neg
	(lb/ton)	-	Neg	-	0.29 (0.03-0.64)[s]	Neg	-	Neg
Sulfur dioxide[s]								
Uncontrolled	(kg/Mg)	-	Neg	40 (36-44)[m]	27 (9-55)[g]	-	-	-
	(lb/ton)	-	Neg	80 (71-88)[m]	53 (18-110)[g]	-	-	-
Emission Factor Rating		E		C	C	C	E	C

[a] Neg = negligible. Dash = not available. Ranges in parentheses.

[b] Reference 1. Estimated from sweating furnace emissions from nonlead secondary nonferrous processing industries. Based on quantity of material charged to furnace.

[c] Reference 1.

[d] Blast furnace emissions are combined flue gases and associated ventilation hood streams (charging and tapping).

[e] Particulate and lead factors based on quantity of lead product produced, except as noted.

[f] Determined negligible, based on average baghouse control efficiency >99%.

[g] References 8-11.

[h] References 8,11-12.

[j] Reference 13. Lead content of kettle refining emissions is 40% and of casting emissions is 36%.

[k] References 1-2. Essentially all product lead oxide is entrained in an air stream and subsequently recovered by baghouse with average collection efficiency >99%. Factor represents emissions of lead oxide that escape a baghouse used to collect the lead oxide product. Based on the amount of lead produced and represents approximate upper limit for emissions.

[m] References 6,8-11.

[n] References 6,8,11-12,14-15.

[p] References 3,5. Based on assumption that uncontrolled reverberatory furnace flue emissions are 23% lead.

[q] Reference 13. Uncontrolled reverberatory furnace flue emissions assumed to be 23% lead. Blast furnace emissions have lead content of 34%, based on single uncontrolled plant test.

[r] Reference 13. Blast furnace emissions have lead content of 26%, based on single controlled plant test.

[s] Based on quantity of material charged to furnaces.

TABLE 7.11-2. FUGITIVE EMISSION FACTORS FOR SECONDARY LEAD PROCESSING[a]

EMISSION FACTOR RATING: E

Operation	Particulate		Lead	
	kg/Mg	lb/ton	kg/Mg	lb/ton
Sweating	0.8 - 1.8	1.6 - 3.5[b]	0.2 - 0.9	0.4 - 1.8[c]
Smelting	4.3 - 12.1	8.7 - 24.2	0.88 - 3.5[d]	1.75 - 7.0[d]
Kettle refining	0.001	0.002	0.0003[d]	0.0006[d]
Casting	0.001	0.002	0.0004[d]	0.0007[d]

[a] Reference 16. Based on amount of lead product, except for sweating, which is based on quantity of material charged to furnace. Fugitive emissions estimated to be 5% of uncontrolled stack emissions.

[b] Reference 7. Sweating furnace emissions estimated from nonlead secondary nonferrous processing industries.

[c] References 3,5. Assumes 23% lead content of uncontrolled blast furnace flue emissions.

[d] Reference 13.

Emissions from battery breaking are mainly of sulfuric acid mist and dusts containing dirt, battery case material and lead compounds. Emissions from crushing are also mainly dusts.

Emissions from sweating operations are fume, dust, soot particles and combustion products, including sulfur dioxide (SO_2). The SO_2 emissions come from combustion of sulfur compounds in the scrap and fuel. Dusts range in particle size from 5 to 20 micrometers, and unagglomerated lead fumes range from 0.07 to 0.4 micrometers, with an average diameter of 0.3. Particulate loadings in the stack gas from reverberatory sweating range from 3.2 to 10.3 grams per cubic meter (1.4 to 4.5 grains per cubic foot). Baghouses are usually used to control sweating emissions, with removal efficiencies exceeding 99 percent. The emission factors for lead sweating in Table 7.11-1 are based on measurements at similar sweating furnaces in other secondary metal processing industries, not on measurements at lead sweating furnaces.

Reverberatory smelting furnaces emit particulate and oxides of sulfur and nitrogen. Particulate consists of oxides, sulfides and sulfates of lead, antimony, arsenic, copper and tin, as well as unagglomerated lead fume. Particulate loadings range from to 16 to 50 grams per cubic meter (7 to 22 grains per cubic foot. Emissions are generally controlled with settling and cooling chambers, followed by a baghouse. Control efficiencies generally exceed 99 percent. Wet scrubbers are sometimes used to reduce SO_2 emissions. However, because of the small particles emitted from reverberatory furnaces, baghouses are more often used than scrubbers for particulate control.

Two chemical analyses by electron spectroscopy have shown the particulate to consist of 38 to 42 percent lead, 20 to 30 percent tin, and about 1 percent zinc.[17] Particulate emissions from reverberatory smelting furnaces are estimated to contain 20 percent lead.

TABLE 7.11-3. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR BAGHOUSE CONTROLLED BLAST FURNACE FLUE GASES[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	93.0	0.22	0.45
10	89.0	0.21	0.43
6	83.5	0.20	0.40
2.5	71.0	0.17	0.34
1.25	44.5	0.11	0.21
1.00	33.0	0.08	0.16
0.625	14.5	0.03	0.07
Total	100.0	0.24	0.48

[a] Units are for lead, as produced.

[b] Expressed as equivalent aerodynamic particle diameter.

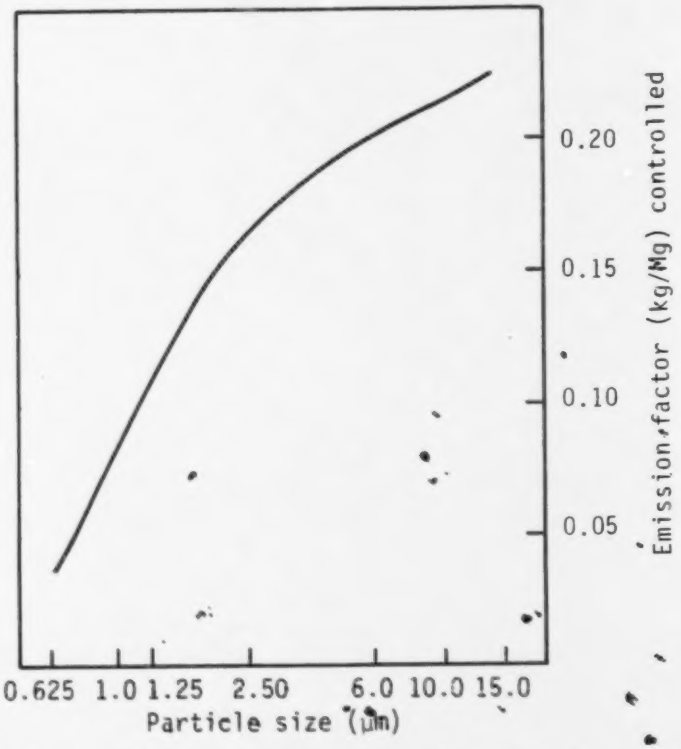

Figure 7.11-2. Emission factors less than stated particle size for baghouse controlled blast furnace flue gases.

TABLE 7.11-4. EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR UNCONTROLLED AND BAGHOUSE CONTROLLED BLAST FURNACE VENTILATION[a]

EMISSION FACTOR RATING: D

Particle size[b] (um)	Cumulative mass % ≤ stated size		Cumulative emission factors			
			Uncontrolled		Controlled	
	Uncontrolled	Controlled	kg/Mg	lb/ton	kg/Mg	lb/ton
15	40.5	88.5	25.7	51.4	0.41	0.83
10	39.5	83.5	25.1	50.2	0.39	0.78
6	39.0	78.0	24.8	49.5	0.36	0.73
2.5	35.0	65.0	22.2	44.5	0.30	0.61
1.25	23.5	43.5	14.9	29.8	0.20	0.41
1.00	16.5	32.5	10.5	21.0	0.15	0.30
0.625	4.5	13.0	2.9	5.7	0.06	0.12
Total	100.0	100.0	63.5	127.0	0.47	0.94

[a] Based on lead, as produced. Includes emissions from charging, metal and slag tapping.

[c] Expressed as equivalent aerodynamic particle diameter.

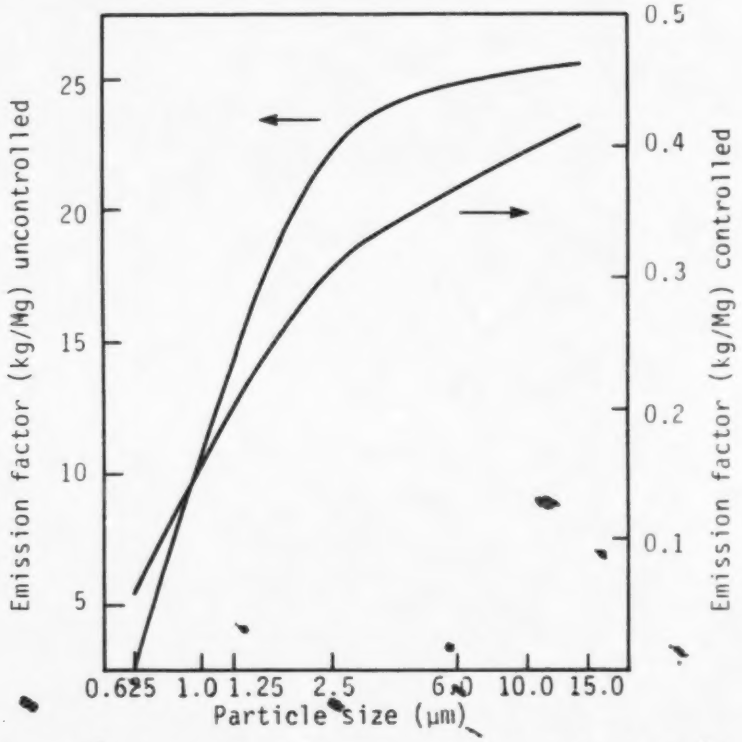

Figure 7.11-3. Emission factors less than stated particle size for uncontrolled and baghouse controlled blast furnace ventilation.

TABLE 7.11-5. EFFICIENCIES OF PARTICULATE CONTROL EQUIPMENT ASSOCIATED WITH SECONDARY LEAD SMELTING FURNACES

Control equipment	Furnace type	Control efficiency (%)
Fabric filter[a]	Blast	98.4
	Reverberatory	99.2
Dry cyclone plus fabric filter[a]	Blast	99.0
Wet cyclone plus fabric filter[b]	Reverberatory	99.7
Settling chamber plus dry cyclone plus fabric filter[c]	Reverberatory	99.8
Venturi scrubber plus demister[d]	Blast	99.3

[a] Reference 8.
[b] Reference 9.
[c] Reference 10.
[d] Reference 14.

Particle size distributions and size specific emission factors for blast furnace flue gases and for charging and tapping operations, respectively, are presented in Tables 7.11-3 and 7.11-4, and Figures 7.11-2 and 7.11-3.

Emissions from blast furnaces occur at charging doors, the slag tap, the lead well, and the furnace stack. The emissions are combustion gases (including carbon monoxide, hydrocarbons, and oxides of sulfur and nitrogen) and particulate. Emissions from the charging doors and the slag tap are hooded and routed to the devices treating the furnace stack emissions. Blast furnace particulate is smaller than that emitted from reverberatory furnaces and is suitable for control by scrubbers or fabric filters downstream of coolers. Efficiencies for various control devices are shown in Table 7.11-5. In one application, fabric filters alone captured over 99 percent of the blast furnace particulate emissions.

Particulate recovered from the uncontrolled flue emissions at six blast furnaces had an average lead content of 23 percent.[3,5] Particulate recovered from the uncontrolled charging and tapping hoods at one blast furnace had an average lead content of 61 percent.[13] Based on relative emission rates, lead is 34 percent of uncontrolled blast furnace emissions. Controlled emissions from the same blast furnace had lead content of 26 percent, with 33 percent from flues, and 22 percent from charging and tapping operations.[13] Particulate recovered from another blast furnace contained 80 to 85 percent lead sulfate and lead chloride, 4 percent tin, 1 percent cadmium, 1 percent zinc, 0.5 percent antimony, 0.5 percent arsenic, and less than 1 percent organic matter.[18]

Kettle furnaces for melting, refining and alloying are relatively minor emission sources. The kettles are hooded, with fumes and dusts typically vented to baghouses and recovered at efficiencies exceeding 99 percent. Twenty measurements of the uncontrolled particulates from kettle furnaces showed a mass median aerodynamic particle diameter of 18.9 micrometers, with particle size ranging from 0.05 to 150 micrometers. Three chemical analyses by electron spectroscopy showed the composition of particulate to vary from 12 to 17 percent lead, 5 to 17 percent tin, and 0.9 to 5.7 percent zinc.[16]

Emissions from oxidizing furnaces are economically recovered with baghouses. The particulates are mostly lead oxide, but they also contain amounts of lead and other metals. The oxides range in size from 0.2 to 0.5 micrometers. Controlled emissions have been estimated to be 0.1 kilograms per megagram (0.2 pounds per ton) of lead product, based on a 99 percent efficient baghouse.

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AP-42 Section 7.7

Primary Zinc Smelting

7.7 PRIMARY ZINC SMELTING

7.7.1 Process Description[1-2]

Zinc is found primarily as the sulfide ore sphalerite (ZnS). Its common coproduct ores are lead and copper. Metal impurities commonly associated with ZnS are cadmium (up to 2 percent) and minor quantities of germanium, gallium, indium and thalium. Zinc ores typically contain from 3 to 11 percent zinc. Some ores containing as little as 2 percent are recovered. Concentration at the mine brings this to 49 to 54 percent zinc, with approximately 31 percent free and uncombined sulfur.

Zinc ores are processed into metallic slab zinc by two basic processes. Four of the five domestic U. S. zinc smelting facilities use the electrolytic process, and one plant uses a pyrometallurgical smelting process typical of the primary nonferrous smelting industry. A general diagram of the industry is presented in Figure 7.7-1.

Electrolytic processing involves four major steps, roasting, leaching, purification and electrolysis, details of which follow.

Pyrometalluirigical processing involves three major steps, roasting (as above), sintering and retorting.

Roasting is a process common to both electrolytic and pyrometallurgical processing. Calcine is produced by the roasting reactions in any one of three different types of roasters, multiple hearth, suspension, or fluidized bed. Multiple hearth roasters are the oldest type used in the United States, while fluidized bed roasters are the most modern. The primary zinc roasting reaction occurs between 640° and 1000°C (1300° and 1800°F), depending on the type of roaster used, and is as follows:

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2 \qquad (1)$$

In a multiple hearth roaster, the concentrate is blown through a series of nine or more hearths stacked inside a brick lined cylindrical column. As the feed concentrate drops through the furnace, it is first dried by the hot gases passing through the hearths and then oxidized to produce calcine. The reactions are slow and can only be sustained by the addition of fuel.

In a suspension roaster, the feed is blown into a combustion chamber very similar to that of a pulverized coal furnace. Additional grinding, beyond that required for a multiple hearth furnace, is normally required to assure that heat transfer to the material is sufficiently rapid for the desulfurization and oxidation reactions to occur in the furnace chamber. Hearths at the bottom of the roaster capture the larger particles, which require additional time within the furnace to complete the desulfurization reaction.

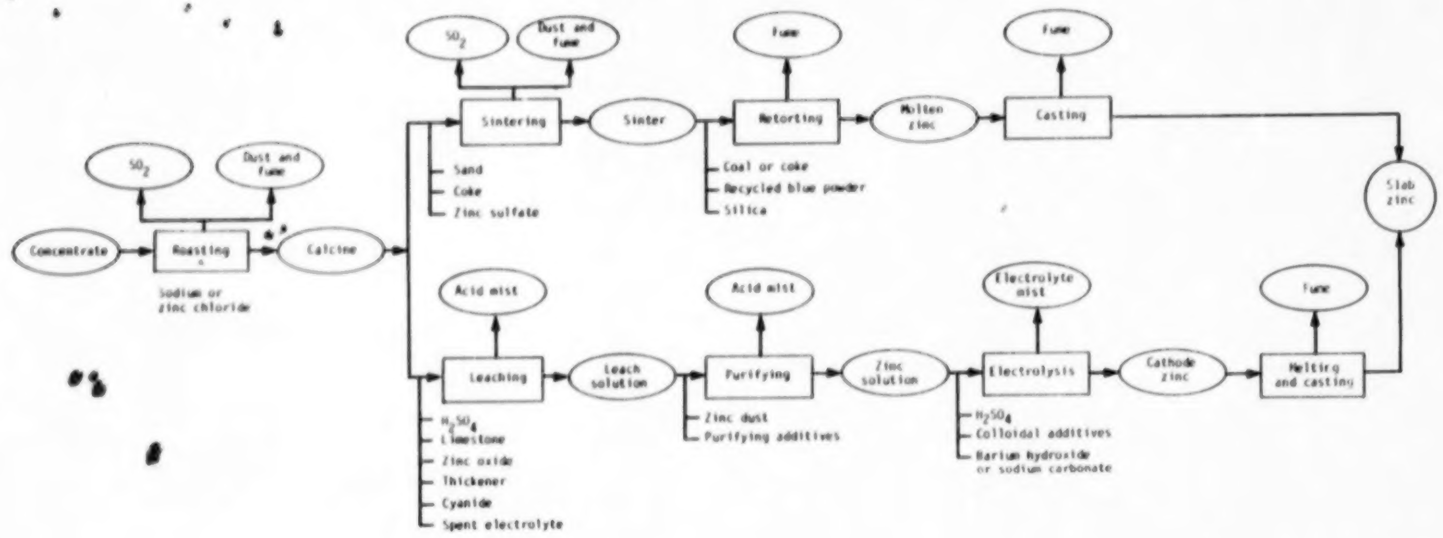
Concentrate
Roasting
Sodium or zinc chloride
SO_2
Dust and fume
Calcine
Sintering
Sand
Coke
Zinc sulfate
SO_2
Dust and fume
Sinter
Retorting
Coal or coke
Recycled blue powder
Silica
Fume
Molten zinc
Casting
Fume
Slab zinc
Leaching
H_2SO_4
Limestone
Zinc oxide
Thickener
Cyanide
Spent electrolyte
Acid mist
Leach solution
Purifying
Zinc dust
Purifying additives
Acid mist
Zinc solution
Electrolysis
H_2SO_4
Colloidal additives
Barium hydroxide or sodium carbonate
Electrolyte mist
Cathode zinc
Melting and casting
Fume

Figure 7.7-1. Typical primary zinc smelting process.

In a fluidized bed roaster, finely ground sulfide concentrates are suspended and oxidized within a pneumatically supported feedstock bed. This achieves the lowest sulfur content calcine of the three roaster designs.

Suspension and fluidized bed roasters are superior to the multiple hearth for several reasons. Although they emit more uncontrolled particulate, their reaction rates are much faster, allowing greater process rates. Also, the sulfur dioxide (SO_2) content of the effluent streams of these two types of roasters is significantly higher, thus permitting more efficient and economical use of acid plants to control SO_2 emissions.

Leaching is the first step of electrolytic reduction, in which the zinc oxide reacts to form aqueous zinc sulfate in an electrolyte solution containing sulfuric acid.

$$ZnO + H_2SO_4 \rightarrow Zn^{+2}(aq) + SO_4^{-2}(aq) + H_2O \qquad (2)$$

Single and double leach methods can be used, although the former exhibits excessive sulfuric acid losses and poor zinc recovery. In double leaching, the calcine is first leached in a neutral or slightly alkaline solution. The readily soluble sulfates from the calcine dissolve, but only a portion of the zinc oxide enters the solution. The calcine is then leached in the acidic electrolysis recycle electrolyte. The zinc oxide is dissolved through Reaction 2, as are many of the impurities, especially iron. The electrolyte is neutralized by this process, and it serves as the leach solution for the first stage of the calcine leaching. This recycling also serves as the first stage of refining, since much of the dissolved iron precipitates out of the solution. Variations on this basic procedure include the use of progressively stronger and hotter acid baths to bring as much of the zinc as possible into solution.

Purification is a process in which a variety of reagents are added to the zinc laden electrolyte to force impurities to precipitate. The solid precipitates are separated from the solution by filtration. The techniques used are among the most advanced industrial applications of inorganic solution chemistry. Processes vary from smelter to smelter, and the details are proprietary and often patented. Metallic impurities, such as arsenic, antimony, cobalt, germanium, nickel and thallium, interfere severely with the electrolyte deposition of zinc, and their final concentrations are limited to less than 0.05 milligrams per liter (4×10^{-7} pounds per gallon).

Electrolysis takes place in tanks, or cells, containing a number of closely spaced rectangular metal plates acting as anodes (made of lead with 0.75 to 1.0 percent silver) and as cathodes (made of aluminum). A series of three major reactions occurs within the electrolysis cells:

$$2H_2O \xrightarrow[\text{anode}]{H_2SO_4} 4H^+(aq) + 4e^- + O_2 \qquad (3)$$

$$2Zn^{+2} + 4e^- \xrightarrow{\text{cathode}} 2Zn \qquad (4)$$

$$4H^+(aq) + 2SO_4^{-2}(aq) \longrightarrow 2H_2SO_4 \qquad (5)$$

Oxygen gas is released at the anode, metallic zinc is deposited at the cathode, and sulfuric acid is regenerated within the electrolyte.

Electrolytic zinc smelters contain a large number of cells, often several hundred. A portion of the electrical energy released in these cells dissipates as heat. The electrolyte is continuously circulated through cooling towers, both to lower its temperature and to concentrate the electrolyte through the evaporation of water. Periodically, each cell is shut down and the zinc is removed from the plates.

The final stage of electrolytic zinc smelting is the melting and casting of the cathode zinc into small slabs, 27 kilograms (60 pounds), or large slabs, 640 to 1100 kilograms (1400 to 2400 pounds).

Sintering is the first stage of the pyrometallurgical reduction of zinc oxide to slab zinc. Sintering removes lead and cadmium impurities by volatilization and produces an agglomerated permeable mass suitable for feed to retorting furnaces. Downdraft sintering machines of the Dwight-Lloyd type are used in the industry. Grate pallets are joined to form a continuous conveyor system. Combustion air is drawn down through the grate pallets and is exhausted to a particulate control system. The feed is a mixture of calcine, recycled sinter and coke or coal fuel. The low boiling point oxides of lead and cadmium are volatilized from the sinter bed and are recovered in the particulate control system.

In retorting, because of the low boiling point of metallic zinc, 906°C (1663°F), reduction and purification of zinc bearing minerals can be accomplished to a greater extent than with most minerals. The sintered zinc oxide feed is brought into high temperature reducing atmosphere of 900° to 1499°C (1650° to 2600°F). Under these conditions, the zinc oxide is simultaneously reduced and volatilized to gaseous zinc:

$$ZnO + CO \rightarrow Zn(vapor) + CO_2 \qquad (6)$$

Carbon monoxide regeneration also occurs:

$$CO_2 + C \rightarrow 2CO \qquad (7)$$

The zinc vapor and carbon monoxide produced pass from the main furnace to a condenser, for zinc recovery by bubbling through a molten zinc bath.

Retorting furnaces can be heated either externally by combustion flames or internally by electric resistance heating. The latter approach, electrothermic reduction, is the only method currently practiced in the United States, and it has greater thermal efficiency than do external heating methods. In a retort furnace, preheated coke and sinter, silica and miscellaneous zinc bearing materials are fed continuously into the top of the furnace. Feed coke serves as the principle electrical conductor, producing heat, and it also provides the carbon monoxide required for zinc oxide reduction. Further purification steps can be performed on the molten metal collected in the condenser. The molten zinc finally is cast into small slabs 27 kilograms (60 pounds), or the large slabs, 640 to 1000 kilograms (1400 to 2400 pounds).

Each of the two zinc smelting processes generates emissions along the various process steps. Although the electrolytic reduction process emits less particulate than does pyrometallurgical reduction, significant quantities of acid mists are generated by electrolytic production steps. No data are currently available to quantify the significance of these emissions.

Nearly 90 percent of the potential SO_2 emissions from zinc ores is released in roasters. Concentrations of SO_2 in the exhaust gases vary with the roaster type, but they are sufficiently high to allow recovery in an acid plant. Typical SO_2 concentrations for multiple hearth, suspension, and fluidized bed roasters are 4.5 to 6.5 percent, 10 to 13 percent, and 7 to 12 percent, respectively. Additional SO_2 is emitted from the sinter plant, the quantity depending on the sulfur content of the calcine feedstock. The SO_2 concentration of sinter plant exhaust gases ranges from 0.1 to 2.4 percent. No sulfur controls are used on this exhaust stream. Extensive desulfurization before electrothermic retorting results in practically no SO_2 emissions from these devices.

The majority of particulate emissions in the primary zinc smelting industry is generated in the ore concentrate roasters. Depending on the type of roaster used, emissions range from 3.6 to 70 percent of the concentrate feed. When expressed in terms of zinc production, emissions are estimated to be 133 kilograms per megagram (266 pounds per ton) for a multiple hearth roaster, 1000 kilograms per megagram (2000 pounds per ton) for a fluidized bed roaster, expressed in terms of zinc production. Particulate emission controls are generally required for the economical operation of a roaster, with cyclones and electrostatic precipitators (ESP) the primary methods used. No data are available for controlled particulate emissions from a roasting plant.

Controlled and uncontrolled emission factors for point sources within a zinc smelting plant appear in Table 7.7-1. Sinter plant emission factors should be applied carefully, because the data source is different from the only plant currently in operation in the United States, although the technology is identical. Additional data have been obtained for a vertical retort, although no examples of this type of plant are operating in the United States. Particulate factors also have been developed for uncontrolled emissions from an electric retort and the electrolytic process.

Fugitive emission factors have been estimated for the zinc smelting industry and are presented in Table 7.7-2. These emission factors are based on similar operations in the steel, lead and copper industries.

TABLE 7.7-1. PARTICULATE EMISSION FACTORS FOR PRIMARY SLAB ZINC PROCESSING[a]

Process	Uncontrolled		Emission Factor Rating	Controlled		Emission Factor Rating
	kg/Mg	lb/ton		kg/Mg	lb/ton	
Roasting						
Multiple hearth[b]	113	227	E	-	-	
Suspension[c]	1000	2000	E	4	8	E
Fluidized bed[d]	1083	2167	E	-	-	
Sinter plant						
Uncontrolled[e]	62.5	125	E	-	-	
With cyclone[f]	NA	NA		24.1	48.2	D
With cyclone and ESP[f]	NA	NA		8.25	16.5	D
Vertical retort[g]	7.15	14.3	D	-	-	
Electric retort[h]	10.0	20.0	E	-	-	
Electrolytic process[j]	3.3	6.6	E	-	-	

[a] Based on quantity of slab zinc produced. NA = not applicable. Dash = no data.

[b] References 3-5. Averaged from an estimated 10% of feed released as particulate emissions, zinc production rate at 60% of roaster feed rate, and other estimates.

[c] References 3-5. Based on an average 60% of feed released as particulate emission and a zinc production rate at 60% of roaster feed rate. Controlled emissions based on 20% drop out in waste heat boiler and 99.5% drop out in cyclone and ESP.

[d] References 3,6. Based on an average 65% of feed released as particulate emissions and a zinc production rate of 60% of roaster feed rate.

[e] Reference 3. Based on unspecified industrial source data.

[f] Reference 7. Data not necessarily compatible with uncontrolled emissions.

[g] Reference 7.

[h] Reference 2. Based on unspecified industrial source data.

[j] Reference 13.

TABLE 7.7-2. UNCONTROLLED FUGITIVE PARTICULATE EMISSION FACTORS FOR PRIMARY SLAB ZINC PROCESSING[a]

EMISSION FACTOR RATING: E

Process	Emission factor[b] (kg/Mg)	Emission factor[b] (lb/ton)
Roasting	Negligible	Negligible
Sinter plant[c]		
Wind box	0.12 - 0.55	0.24 - 1.10
Discharge and screens	0.28 - 1.22	0.56 - 2.44
Retort building[d]	1.0 - 2.0	2.0 - 4.0
Casting[e]	1.26	2.52

[a] Based on quantity of slab zinc produced, except as noted.

[b] Reference 8.

[c] From steel industry operations for which there are emission factors. Based on quantity of sinter produced.

[d] From lead industry operations.

[e] From copper industry operations.

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